

DDTs and PCBs in the Adriatic Sea

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A review and discussion of analytical developments in the determination of DDTs and PCBs in sea environment are presented, including sample treatment, clean-up, identification and quantitative determination by gas-liquid chromatography.

The fates of chlorinated hydrocarbons in the sea are discussed with regard to the pollutant-particle association with surfaces and their dynamics in a coastal marine environment. Hydrophobic association of pollutants with surfaces and then their biological incorporation, aggregation and cycling are also discussed.

The levels and trends of DDTs and PCBs in the Adriatic Sea air, rain, water, sediments, plankton, plants, shellfish, crabs, fishes, and other marine organisms, including seabirds and mammals, are reviewed and compared with the levels of these pollutants in the Mediterranean area. Comparison of data reported for DDTs and PCBs levels in different environmental compartments of the Mediterranean and the Adriatic Sea over the last two decades shows a substantial decline in these compounds. The author also presents discussion about the use of biomarkers for risk estimation of micropollutants in the Adriatic and the risk related to acceptable daily intake of chlorinated hydrocarbons by a critical population on the coast.

Key words: Mediterranean Sea, Adriatic Sea, chlorinated hydrocarbons, DDTs, PCBs, analysis, levels and trends, water, sediment, marine organisms, gas chromatography.

INTRODUCTION

The Adriatic Sea is an elongated basin (139 000 km²) of the northern Mediterranean, extending for 800 km into the heartland of the European

continent. On its southern side the Adriatic Sea is connected to the Mediterranean Sea *via* the relatively narrow (70 km) Otranto strait, with a sill depth of about 800 m. Renewal of the Adriatic water has been estimated in the range of 5 to 10 years,^{1,2} which is about ten times shorter than the whole Mediterranean water renewal (70–100 years).^{3,4} Morphologically, the Adriatic Sea can be divided into three parts.⁵ The shallow northern part (max. depth 75 m) extends southwards in a line joining Ancona (Italy) with Pag Island (Croatia). The central part, with the Jabuka Trench (max. depth 270 m), is separated by the Palagruža Sill (130 m) from the deepest southern part (max. depth 1270 m).

The shallow northern Adriatic receives considerable freshwater discharge ($3000 \text{ m}^3 \text{ s}^{-1}$) mainly from the Po River, one of the major rivers in the Mediterranean area (about 50% of the total discharge).⁶ Many minor rivers, streams, and drainage canals flow into the sea from the northern and western coasts, while underground karstic springs and a few karstic streams are scattered along the East Coast. A resident population of 15 million lives in the Po River watershed, on seven million hectares of land, half of which is intensively cultivated. The industrial organic load (expressed in BOD_5) in this region accounts for 40 million inhabitant equivalents.⁷ In addition, significant quantities of wastewater are discharged directly into the sea from the coastal regions, which are densely populated and have well-developed industrial and marine activities. Finally, tourist population increases significantly during the summer period, raising the basic organic load and various pollutants.

During the 1970s, there was increased emphasis on pollution research in the Adriatic in response to increased anthropogenic loads due to the intensive development of agriculture, industry, marine traffic, port activities and tourism in the area. Residues of synthetic chlorinated pesticides and industrial chlorinated hydrocarbons are widespread throughout the terrestrial and oceanic environments due to their resistance to degradation. The toxicological and other harmful effects of these compounds on ecosystems have been well documented.^{8,9} Accumulation of chlorinated compound residues, contributed *via* the atmosphere, may have occurred in the Adriatic Sea, for which water renewal time is less than 10 years. Moreover, additional quantities of these pollutants were added to the sea from various local sources (mainly sewage and industrial wastewater disposal, port activities, agricultural drainage) located on the coast, including semi-enclosed embayments.^{10–13}

The use and application of PCB technical mixtures have led to significant levels of the more common PCBs in almost every aspect of the environment. Concern has increased over the years with regard to the ecotoxicological and human health implications of the environmental presence of

materials containing PCBs. The toxicities of PCBs differ for each congener and range from highly toxic, which are potent inducers of enzymes (P-450) and glucuronyl transferases, to moderately toxic, which are more potent inhibitors of dopamine and other neurotransmitters.¹⁴ PCBs have immunosuppressive activity, are tumor promoters and interfere with calcium utilization (thus producing their well-known negative effect on eggshell formation in birds).¹⁵ Both the EPA and the International Agency for Research on Cancer (IARC) classify them as carcinogens. Because of their persistence, potential for bioaccumulation and biomagnification, monitoring of PCBs is important for the conservation of the environment and biota.

Most measurements and data on chlorinated hydrocarbons in the Adriatic were on the total DDTs (insecticide DDT and its analogues DDE and DDD) and PCBs, which belong to the group of the most persistent organic pollutants. Therefore, this review is focused on these pollutants.

GENERAL FACTS ON ORGANOHALOGEN COMPOUNDS AS CHEMICALS AND POLLUTANTS

Organohalogenes are a group of organic compounds which are substituted by halogens *i.e.* chlorine, bromine, fluorine or iodine. The list of organohalogen compounds, which is believed to be of economical or pollutional importance, consists of more than one thousand substances. Approximately 20% of these are pesticides while the rest are miscellaneous compounds used, produced or by-produced by the industries. A large majority of environmental information available refers to chlorinated hydrocarbons and especially to chlorinated pesticides.^{8,10}

DDT is the abbreviation for dichlorodiphenyl trichloroethane but the correct chemical name for the *p,p'*-isomer is 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane. The technical product usually contains up to 30% of the *o,p'*-isomer and the material is used against a wide variety of agricultural and forest pests and against insect pests including disease vectors such as mosquito and tsetse fly. In the environment DDT can be degraded by solar radiation or metabolized in organisms. Dehydrochlorination gives the metabolite DDE and dechlorination the metabolite DDD.

Polychlorinated biphenyls (PCBs) are a group of aromatic organochlorine industrial products similar in structure to chlorinated hydrocarbon insecticides such as DDT. PCBs are produced commercially by chlorinating biphenyl with anhydrous chlorine. The mixture obtained is purified and, during this process, hydroxylated biphenyls and chlorinated dibenzofurans can be formed. Commercially produced PCBs are mixtures of chlorinated biphenyl isomers and homologues. Impurities found in commercial PCBs

can include polychlorinated naphthalenes (PCNs) and polychlorinated dibenzofurans (PCDFs).¹⁶

PCBs have the empirical formula $C_{12}H_{10}Cl_n$ ($n = 1-10$). There are 209 chlorobiphenyl congeners, which can be divided into nine isomeric groups and decachlorobiphenyl. Although all 209 of the PCB congeners have been synthesized, the reaction conditions in the commercial process tend to favor specific substitution reactions leading to particular compositions of the chlorinated products. Today, some 20 congeners are thought to be absent from all of the technical mixtures.^{17,18} The commercial products – Aroclor (USA), Chlorphen (Germany) and Kaneclor (Japan) – are complex mixtures containing 132 congeners, and each mixture consists of different, but overlapping, assemblages of PCBs. Because of their ubiquity, PCBs are common environmental pollutants that are included in the priority pollutants list published by the US Environmental Protection Agency (EPA) and by the European Union.¹⁹

ANALYTICAL METHODS FOR DETERMINATION OF DDTs AND PCBs IN AQUATIC ENVIRONMENT

Analytical methods commonly used in analyses of chlorinated hydrocarbons in aquatic environment are time consuming, labor-intensive and costly in terms of expensive solvents and absorbents. This is because the investigated pollutants, which are mostly present at parts per billion (ppb) levels in sediments and biota and parts per trillion (ppt) in water, have to be concentrated and separated from the matrix (sample clean-up) so that they can be identified and measured by gas chromatography.

The basic steps of chlorinated hydrocarbons residue analysis are:

- (i) sampling,
- (ii) extraction from the sample,
- (iii) clean up of residues from the sample,
- (iv) identification and quantitative determination.

Many books and papers have been published on the methodology for the analysis of various organic pollutants in aquatic environments. The most recently published reviews on the subject of the analysis of chlorinated hydrocarbons in water and food were published in the *Journal of Chromatography*.^{19,20}

Sampling

Water sampling is difficult because there are usually low concentrations of PCBs in waters due to the hydrophobic nature of these compounds. Con-

centrations in seawater in the low picogram per liter level have been reported for the most abundant PCB congeners. In seawater samples, the concentration of chlorinated hydrocarbons is high in the surface layers. The air-sea interface is a point of interest because sea slicks may significantly accumulate PCBs.²¹⁻²³ There are specific microlayer samplers suitable for collecting the upper water layer of 50–400 μm thickness. For this purpose, different samplers have been designed: the Blumer sampler, the DHI sampler and a high-volume water sampler prepared to pump water from a defined depth below the sea surface outside the wake of the survey vessel.²⁴

Recovery measurements are one of the more difficult and ill-defined aspects of trace organic analysis in environment samples. Experiments designed to obtain the efficiency of an analytical method often implicitly assume that this also includes the efficiency of extraction from the matrix. Differences in behavior between spiked chlorinated hydrocarbons and those already present in the water phase or other biotic or abiotic samples have induced some researchers to perform recovery measurements by comparing several extraction methods.²⁵ In most of the methods the commodity is spiked with the chemical prior to extraction and the percentage recoveries are tested. Such an approach may prove the validity of the clean-up method but it does not evaluate satisfactorily the effectiveness of the extraction procedure. Attempts to distinguish the available and total pollutant levels have involved the use of radiolabelled chemicals to determine the solvent extractable material. For good results, each step requires studies on each sample type, because procedures involving extraction, clean up, separation and quantification are different and specific for each substrate.²⁵

Extraction

Water

The method used for extraction from water is partitioning into an organic solvent to extract the pesticides. Besides the common methods, like liquid-liquid partitioning, some procedures involve extraction of acidified water with hexane. Solid-phase extraction and elution with an organic solvent and use of Sep pak cartridges packed with CN bonded porous silica are some of the methods used.^{19,20,26}

Sediments and Biological Samples

Organochlorine residues may be recovered from biological samples by exhaustive extraction with a variety of organic solvents, such as for example: hexane, ether, acetone, alcohol and their combinations. The methodology varies from simply standing (keeping) the commodity in a solvent overnight

to a more exhaustive technique such as Soxhlet extraction. Sample material with a low-fat and wax content can be extracted directly, separated and analyzed by gas chromatography. Extracts of many samples may contain large amounts of fats and pigments, which will remain after the extract has been evaporated. This will result in low sensitivity, poor response and may even damage the column packing.

In all the extractions, especially for the multi-residue type, use of high purity reagents and solvents helped to minimize interference problems. The impurity levels of all solvents and reagents used did not exceed an acceptable blank when subjected to the complete procedure without the sample.²⁷

Clean-up Extracts from Various Commodities

Clean up is an essential step for accurate determination of pesticide residues, but many conventional methods are costly and time consuming. Clean-up techniques currently include liquid-liquid partitioning, open column chromatography, thin-layer chromatography, steam distillation and low temperature precipitation. Of the several new approaches successfully used in modern methodology, use of small columns is the most notable.^{28,29}

Commonly used methods for the clean-up of raw extracts of samples are chromatographic columns filled with an adsorbent such as florisil, alumina, silica gel, mixtures of alumina and silica gel, gel permeation on Bio-Beads SX3.

Considering that several organochlorines are present together, a crude separation into groups may be effected using various types of column chromatography. Treatment of extracts with sulfuric acid is another way of clean-up. It is used especially for removing fats.

Determination by Gas-liquid Chromatography

Gas-liquid chromatography (GLC) is one of the most important analytical techniques used in chlorinated hydrocarbon residue analysis. Two advantages are its sensitive and specific detector system and its ability to separate the mixture of analytes on the column. Until recently, GLC of pesticides was conducted using packed columns containing a variety of liquid phases and supports. An electron capture detector is equipped to determine low amounts of residues from small samples of various substrates. As total reliance should not be placed on the analytical data obtained from GLC for the identification of a pesticide residue, it is necessary to compare it with other methods like GC-MS and GLC using alternate column packings.^{18,19}

The capillary columns in gas chromatography have been applied to the analysis of environmental samples for high resolution or separation of iso-

mers of many pollutants. These columns are wall coated with a thin film of liquid phase which produces a large number of theoretical plates so that high resolution of analytes is possible. They provide an inert surface, preventing column decomposition or adsorption and low temperature programming to produce sharp fundamental peaks without excessive baseline desorption and retention times that are not too long.

The recent advance is the use of dual-column dual-detector gas chromatographic determination³⁰ and two-dimensional capillary gas chromatography with three detectors in parallel.³¹

Use of Internal Standards and Confirmation

Retention times are difficult to reproduce due to the inevitably slight changes in experimental conditions; hence retention times are best expressed as values related to the retention time of a standard reference compound included in the same chromatogram. Aldrin and Mirex can be used as an internal standard for organochlorines since they have intermediate retention times and relative retention times. The internal standard is still used for minimizing error arising from other contaminants.^{32,33}

Chemical derivatization serves as a method for the identification and confirmation of pesticide residues. The recent trend is the use of GC-MS for the multi-residue determination.³³

Special Problem of the PCB Congener Determination

The PCB problem was recognized over 20 years ago, resulting in extensive reports and reviews on environmental contamination levels. However, only a small proportion of these studies discussed the distribution and occurrence of individual PCBs as part of the analysis of environmental samples.³⁴⁻³⁶ Although the approach to PCB determination has rapidly changed in recent years, it is still easy to understand the historical reasons for the inertia in measuring individual congeners. Total PCB levels are often required for legislative monitoring programs and for the measurement of environmental effects caused by the PCB formulations as such. Early analytical techniques using packed column gas chromatography could only measure »total PCB« content by summing up the few-seemingly, fully-resolved peaks, or by conversion of all PCBs into a single compound. Only with the development of high-resolution capillary gas chromatography with electron capture detection and/or mass spectrometry has it become possible to determine more accurately the presence of individual PCBs on a routine basis.³⁷⁻³⁹

Although the determination of planar PCBs follows the same general route as for the other, more abundant PCBs, *viz.* extraction, clean-up and

group separation prior to the final determination by GC with either ECD or MS with multiple ion detection, the presence of these compounds in the environment at ultra-trace concentrations ($1\text{--}10\text{ pg g}^{-1}$) requires significant refining of the normal routine methods. Kannan *et al.*³⁸ have determined the planar PCBs in several commercial Aroclor mixtures: they found $260\text{--}6100\text{ }\mu\text{g g}^{-1}$ for PCB 77, $8.6\text{--}62\text{ }\mu\text{g g}^{-1}$ for PCB 126 and $0.05\text{--}0.51\text{ }\mu\text{g g}^{-1}$ for PCB 169. Seawater in the open ocean may contain as little as $0.03\text{--}1.0\text{ ng dm}^{-3}$ of total PCBs, which would lead to as little as 0.001 pg dm^{-3} of planar PCBs. This concentration is well below the detection limits and would require an initial sample size of $100\text{ }000\text{ dm}^3$ in order to approach these limits. The size of a sediment sample required for analysis is, of course, also dependent on the degree of contamination. Relatively clean open sea sediments may have PCB levels in the range of $1\text{--}5\text{ ng g}^{-1}$. At this background level of PCBs, it may be necessary to take a sample size of up to 10 kg for extraction in order to meet the detection limits for the planar PCBs. The sample weight can be reduced substantially by using a micro reversed-phase LC column directly coupled to the capillary GC system through an interface consisting of an on-column injector and a retention gap. These systems have been used successfully for the enrichment of PCBs and pesticides from aqueous and sediment samples at the ppt level, since they allow one to use injection volumes of up to 1 ml . Sample pretreatment may be much shorter when these systems are used, and the time of analysis can be reduced to the time of the GC run.¹⁷

In several European countries, monitoring of selected congeners took the place of monitoring »total PCB« levels in environmental programs. In West Germany and in the Netherlands, determination of individual congeners is statutorily regulated for the control of waste mineral oils. A set of six or seven congeners is habitually used for monitoring.^{17,40}

Intercalibration

Applicability of monitoring data depends on their quality measured in terms of reliability, which depends on precision (reproducibility) and accuracy (true values). The accuracy of the results is evaluated applying participation in intercomparison runs with the samples of composition similar to the environmental samples. To improve the reliability and accuracy of the obtained monitoring data, participating institutions have taken part in standardization and intercalibration exercises organized on national or international levels. Since 1973, the Monaco Laboratory of IAEA has organized regular intercomparison exercises on a global and regional scale.⁴¹

In a report issued by IAEA MEL,⁴² the quality of the analytical data for the MED POL programs over a 19-year period (1973–1993) was evaluated.

Of the institutions from which data on the DDTs and PCBs in the Adriatic Sea have been published, six laboratories from Croatia, two from Slovenia and four from Italy participated in the intercalibration exercises. In the period from 1976 to 1988, the laboratory of the Center for Marine Research, Zagreb, Ruđer Bošković Institute (CMR-Z) was the only Croatian laboratory that regularly participated in the intercalibration exercises for trace organochlorine compounds during all nine intercomparison runs.

Based on the frequency of participation and the quality of the data reported, the IAEA has issued a list of selected laboratories around the Medi-

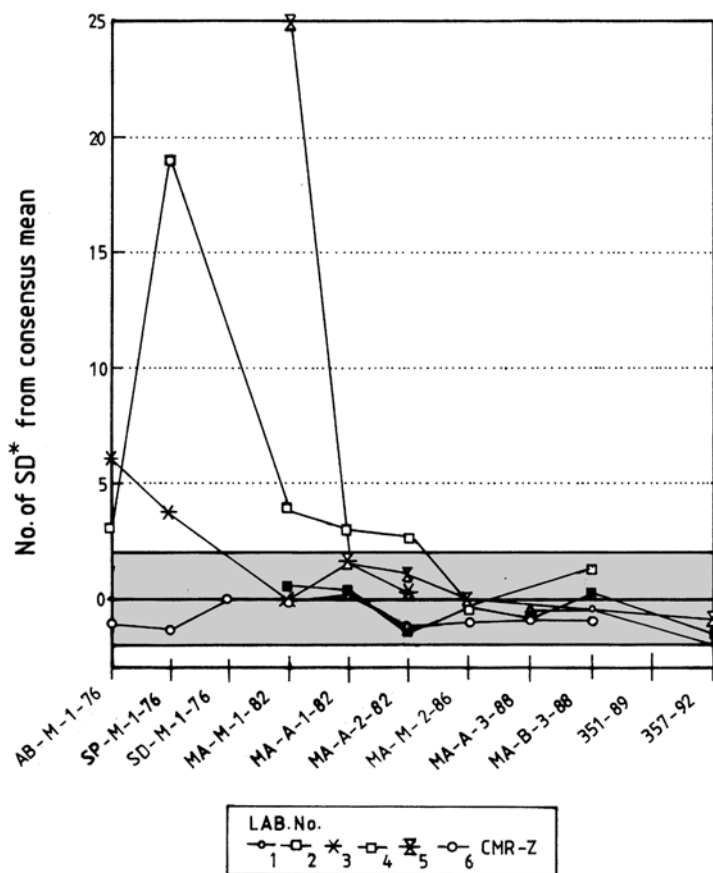


Figure 1. Development of data quality for Aroclor 1254 content in samples of marine water (XAD-2 extract) organisms and sediment in selected MED POL laboratories (modified from Mee *et al.*).⁴² SD represents standard deviation based on the results of the world-wide intercomparison exercise. Shaded area indicates data within the control limits. Data of Center for Marine Research, Ruđer Bošković Institute, Zagreb, Croatia (CMR-Z).

terranean for trace organochlorine compound analysis.⁴² Of the 56 laboratories from 14 Mediterranean countries that participated in the intercalibration runs to determine chlorinated hydrocarbons in marine samples, six were selected for their excellent analytical performance. Among them, only the Center for Marine Research, Zagreb (CMR-Z) and the Institute of Marine Biology, Venice, Italy, published most data on chlorinated hydrocarbons in the Adriatic Sea.

For the purpose of this overview, the data on Aroclor 1254 in the marine water (XAD-2 extract), biota and sediment samples are presented in Figure 1 (Fig. 18 from the publication by Mee *et al.*, 1993).⁴² As seen from Figure 1, only data from three of the six »reference« laboratories have never exceeded the control limits.

SOURCES AND FATE OF DDTs AND PCBs IN THE MARINE ENVIRONMENT

Sources

There are no sales or production statistics on chlorinated pesticides and PCBs for the Mediterranean countries. Within the framework of the MED POL X of the MED POL Phase I Program, consumption figures on the total chlorinated pesticides and DDTs were collected for the 1973–1976 period, as presented in Table I.⁴³

Inputs into the Sea

Atmosphere

The discovery of DDTs and other chlorinated hydrocarbons in many parts of the world oceans far from apparent direct input, shows that the mechanisms of global dispersion of some of these pollutants had to be by a more rapid mode than it was possible by oceanic turbulence and current systems. The trans-Atlantic atmospheric transport of DDT by the Northeast Trade Wind System was first deduced from observations of Risebrough *et al.*⁴⁴ Comparison of atmospheric and riverine input rates of organohalogen compounds to the World Ocean made by GESAMP⁴⁵ shows that pollution of the marine environment by these substances through the atmosphere is more important than that through river discharges.

In the Mediterranean Sea, atmospheric polychlorinated biphenyls were monitored over a two-year period at a coastal sampling station in Monaco and from ships.⁴⁶ Levels of PCBs in the near ocean atmosphere in Monaco are in a range from 0.03 to 0.96 ng m⁻³, in the western Mediterranean basin

TABLE I
Pesticide consumption by agriculture in the Mediterranean watershed (modified from UNEP/FAO/WHO/IAEA, 1990)⁴³

Kind of pesticide	Consumption (active ingredient / t per year)											Estimated area treated 10 ³ km ²	
	Cyprus (1976)	Egypt (1975/76)	Greece (1973)	Israel (1974)	Italy ^a (1975)	Lebanon (1973)	Libya (1974)	Spain ^b (1976)	Syria ^b (1976)	Tunisia (1973/74)	Turkey (1976)		TOTAL
Organochlorine compounds	14.9	743.3	85.5	132.3	2972.4	35.3	5.8	323.2	65.8	39.0	1266.8	5684.3	216.8
DDT and related compounds	11.2	169.3	—	10.3	866.4	—	—	12.7	36.7	—	864.1	1970.7	29.1

^a Except Piemonte, Valle d'Aosta, Lombardia, Trentino, Alto Adige and Umbrian regions.

^b Mediterranean watershed only.

from 0.05 to 0.30, in the Tyrrhenian Sea 0.1, in the Ligurian Sea 0.3, and in the Adriatic Sea from 0.04 to 0.10 ng m⁻³.

Airborne particulate matter was continuously sampled from the atmosphere of the residential town area of Ljubljana and trapped on a filter. The PCB level in the particulate matter in the atmosphere was 1.3 ng m⁻³ and the total DDT concentration was 0.86 ng m⁻³. Since gaseous forms of chlorinated hydrocarbons were not effectively trapped, true atmospheric levels could have been considerably higher than those actually reported.⁴⁷

The levels of PCBs and chlorinated pesticides were measured in some samples of rainwater collected during 1979/80 in Rijeka, Croatia,⁴⁸ and in the south of France, Menton.⁴⁹ Levels of pollutants are in line with those reported in the world literature for other areas.

Single PCB congeners, DDT and its metabolites were determined in rainwater from different areas of Northern Italy in recent years. Differences were observed both in terms of PCB profiles and of PCB and DDT levels. Pollution levels were not ascribable to long distance transport alone. Both in the case of DDT compounds and in the case of PCB congeners, local input into the environment can be supposed.⁵⁰

Other Discharges

Beside atmospheric deposition, halogenated hydrocarbons reach the marine environment through agricultural run-off, rivers and discharge of industrial and municipal wastes. Measurements of organochlorines in the particulate and dissolved phases of the River Ebro water in northeastern Spain, sampled at the mouth in four periods between 1982–1983, are combined with data on daily flows to produce estimates of the inputs of these compounds into the northwestern Mediterranean from this source. Relatively high levels of *p,p'*-DDT among the DDT compounds indicated recent use or mobilization of DDT. These estimates of river inputs of these contaminants are substantially lower than those used or derived in several recent reviews of contamination problems in the Mediterranean; they support the conclusions of other studies that the principal dispersal pathway of the organochlorines is the atmosphere. The UNEP review⁵¹ of pollutants from land-based sources in the Mediterranean estimated that the load of persistent organochlorine compounds carried by surface run-off directly or through rivers into the Mediterranean Sea is about 90 t per year. Earlier estimates by MEDPOL X in 1976–1977 of the total load of chlorinated biocides, excluding PCBs, entering the Mediterranean from land-based sources were in the order of 50–200 t per year. Relatively few measurements of organochlorines in river waters, however, were used in developing these estimates. The Ebro accounts for about 6% of the fresh water entering the Mediterranean from rivers; if the organochlorine levels reported for the

Ebro are typical of the majority of Mediterranean rivers, the total input of organochlorines from rivers would be somewhat less than 2 t. The estimate derived by UNEP^{51,52} for the persistent organochlorines carried by surface run-off directly or through rivers⁵² was 90 t per year.

Figure 2 shows the amounts (in mg s^{-1}) of chlorinated pesticides that were carried by the River Po⁴³ in January, April and July 1973. Galassi *et al.* investigated polychlorinated biphenyls (PCBs) and chlorinated pesticides

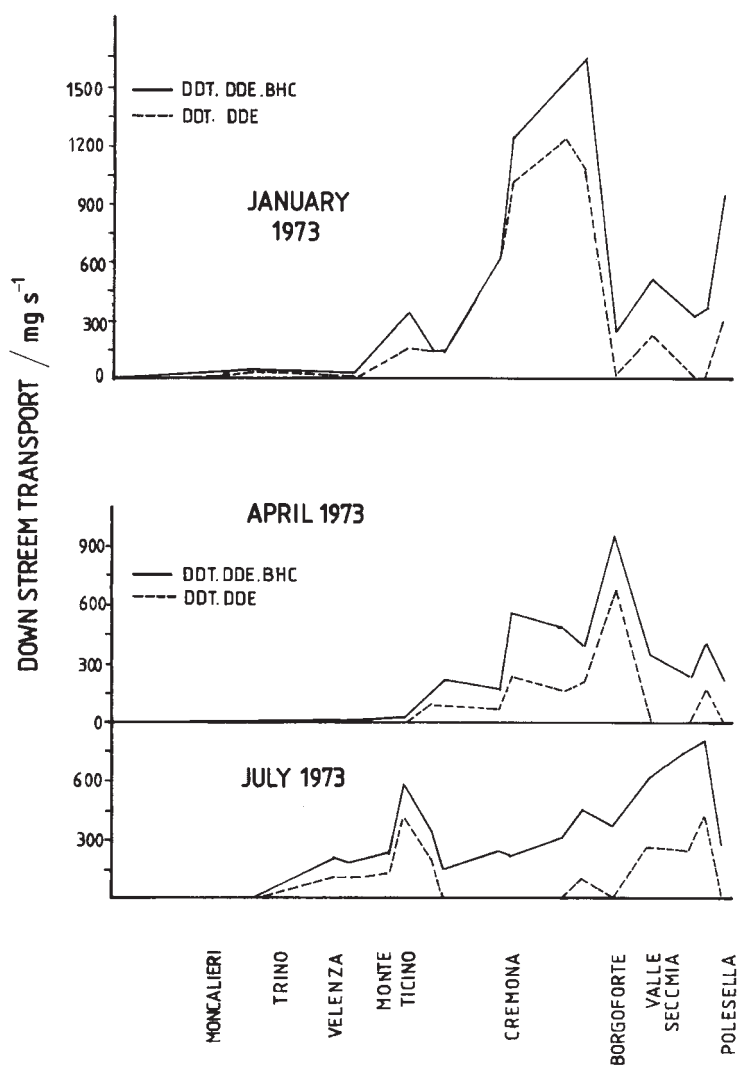


Figure 2. Downstream transport of chlorinated hydrocarbons in the River Po (modified from UNEP/FAO/WHO/IAEA).⁴³

in several organisms and in the sediment sampled in the final stretch of the River Po.⁵⁴

The Tagliamento River drains a land surface of 2 580 km², of which 2 293 km² extends on mountains, and flows into the northern Adriatic Sea. Cultured land (vineyards, orchards and arable land) represents only 29% of the watershed. The total load of chlorinated hydrocarbons delivered by the Tagliamento River, estimated on the basis of their mean concentrations

TABLE II

Average, minimum and maximum concentrations of chlorinated hydrocarbons in wastewaters and sewage sludge

Location and year	Compounds	Concentration / $\mu\text{g dm}^{-3}$			Refs.
		average	min.	max.	
Great Britain, sewage effluents	DDT	36	ND ^a	130	58
Great Britain, sewage effluents	DDT	131 (21) ^b	ND	800	59
Canada, Southern Ontario, raw sewage (5 cities)	PCBs	2.0 (8)	0.6	4.4	60
Canada, Hamilton (raw sewage)	PCBs	10.8 (38)	1.5	27.3	61
	DDT		36000	130000	
Canada, Hamilton (sewage sludge) ^c	PCBs		40	5000	
	DDT		10000	500000	
Los Angeles County tertiary treatment system, 1978, effluents	DDTs	ND			62
Tokyo treatment plants (4 plants)	PCBs	ND			63
Ispra standard sewage sludge	PCBs	2600 (4)	1150	4900	64
Aluminium smelt wastewater from sedimentation basin	Decachloro-biphenyl	54			65
Cortiu, France (Urban sewage-outlet point, 1984)	PCBs	0.057			66
Adriatic, Rijeka town wastewaters, 1986	PCBs	0.008 (12)	ND	0.027	11
	DDTs	0.069 (12)	ND	0.223	

^a ND, not detected (under sensitivity limit).

^b Number of samples in brackets.

^c Values presented as the mass fraction ($w \times 10^9$) of compound(s) in sewage sludge.

and a mean flow of $62 \text{ m}^3 \text{ s}^{-1}$, was: 3.3 kg a^{-1} for HCH, 1.8 kg a^{-1} for DDT, 10.2 kg a^{-1} for PCBs.^{55,56,57}

Although many baseline studies were conducted in the Adriatic and Mediterranean ecosystems, only a few data on chlorinated hydrocarbon concentrations in wastewater entering the Adriatic and even other Mediterranean areas were found in the available literature. Table II shows some data on concentrations of chlorinated insecticides and PCBs in various wastewaters the world. As seen, the presented ranges of concentrations are extremely high: from »non detected« (varying and depending on the analytical methodology) to the values reaching $130\,000 \mu\text{g dm}^{-3}$ for DDTs and from ND to $4900 \mu\text{g dm}^{-3}$ for PCBs.

The presence of some chlorinated hydrocarbon pesticides at concentrations ranging from 0.19 (BHC) to $0.95 (p,p'\text{-DDE}) \mu\text{g dm}^{-3}$ in slaughter wastewater was observed in Alexandria.⁵³ Samples of wastewaters were collected between 1976 and 1987 at several stations located in the Rijeka Bay, Croatia. Concentrations of chlorinated insecticides and polychlorinated biphenyls in a range from < 0.2 to 657.2 ng dm^{-3} for DDTs and from < 0.3 to $9115.5 \text{ ng dm}^{-3}$ for PCBs were found.¹¹

The Fate of Chlorinated Hydrocarbons in the Sea

Despite the difficulties associated with the analysis of organochlorine compounds, especially at the low concentrations normally found in marine samples, there is now little doubt that the chlorinated hydrocarbons such as DDT, dieldrin and PCBs, are major long-term contaminants of the total environment and small traces can be found in almost all compartments of the world ecosystem.⁶⁷ An attempt to summarize the cycling of pesticides through the environment is made in Figure 3, which illustrates the movements of residues through the various compartments of the environment.

Pollutant-particle Association with Surfaces and Dynamics in the Coastal Marine Environment

A wide variety of substances, including chlorinated hydrocarbons, become associated with »particles« in the coastal marine environment. This association may result from:

- (i) precipitation or hydrophobic interactions with the particle surface,
- (ii) co-precipitation with hydrous oxides or iron and manganese either as coatings, or as flocs of the precipitate,
- (iii) incorporation into mineral lattices, organisms or faecal material, or
- (iv) flocculation of colloidal organic and inorganic matter during river and sewage mixing.⁶⁸

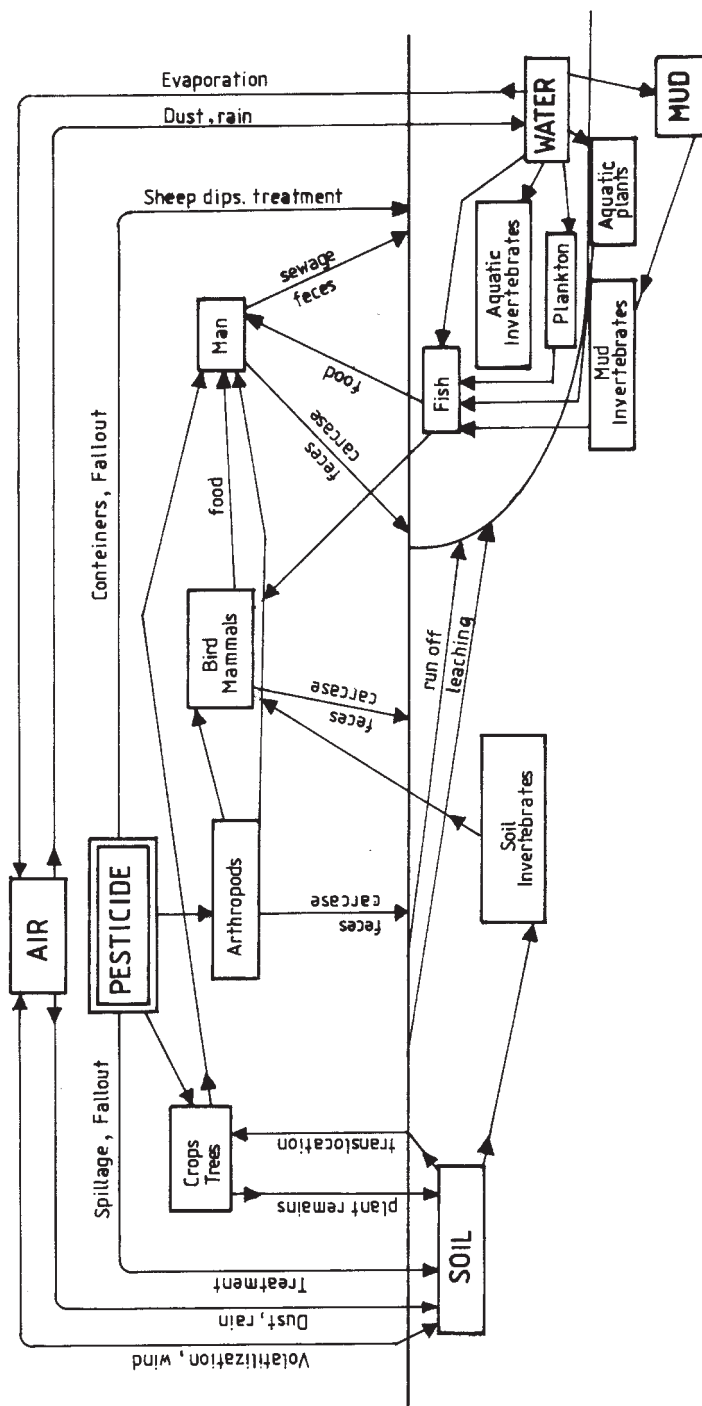


Figure 3. Movement of pesticides between environmental compartments (modified from Edwards).⁶⁷

Hydrophobic Association with Surfaces

The distribution coefficient for a specific pollutant may vary in dependence on the chemical form and concentration of that pollutant. Bopp⁶⁹ showed that the lower-chlorinated biphenyls (di- and trichlorobiphenyls) have a lower distribution coefficient ($< 10^4$) relative to the higher-chlorinated biphenyls (penta- and hexachlorobiphenyls), which have a K_d value of the order of 10^{-5} .

The equilibrated distribution of DDTs between its liquid and solid phases in the Adriatic seawater medium was investigated by means of the radiotracer seawater technique.^{70,71} These various investigations examined the influence of DDT concentration on its adsorption on several model solid phases and the marine sediments. Desorption experiments indicated that the adsorption process is reversible. Desorption was higher from quartz than from limestone, and was significantly lower from marine sediments. Examination of the equilibrium distribution of DDT between sea water and the examined surfaces suggested that DDT existed as a colloidal dispersion in the investigated systems. Investigations of the fate of DDT and its metabolized DDE and DDD as well as dieldrin and Aroclor 1254 (PCB) in laboratory-grown phytoplankton cultures have been described by Picer *et al.*,⁷² and tend to confirm this suggestion.

In order to evaluate the effects of municipal waste-waters on communities, one of two experimental basins in the lagoon of Strunjan (North Adriatic, Piran) was treated with 300 dm³ of primary settled sewage daily, while the other was kept clean as control.⁷³ The resulting accumulation of organochlorine compounds in sediments of the polluted basin were found to be higher than in the clean one. The sum of the DDT and DDT derivatives was approximately three times higher in the polluted basin than the values obtained in the clean basin. The same applied to PCBs. Similar trends were also found in mussels and holothuria, but this was not the case of crabs, which are both predators and scavengers.

Biological Incorporation, Aggregation and Cycling

Biological incorporation, aggregation and incorporation into biogenic particles, coupled with subsequent organism migration, food chain transfer, or faecal pellet deposition, provides a rapid and ecologically important transport system in the marine environment. Pollutant associations with organisms are a result of direct uptake from ingestion of sediment particles, organic-pollutant complexes or contaminated food or passive sorption as water passes over gills, mucous layers, tests, or other exposed surfaces.⁷⁴ The rate of vertical mixing in the ocean is too slow to account for the quantities

of polychlorinated biphenyls found in Mediterranean abyssal sediments if one assumes that they penetrate into the deep ocean only in the dissolved state.⁷³ An alternative explanation is that PCBs are carried to the sediments by rapidly sinking particles.

Setting particles collected in semi-permanent particle interceptor devices (PITS) at a 100 m depth in a water column of 250 m, 2 km off the Monaco coast in the north western Mediterranean, were analyzed for petroleum and chlorinated hydrocarbons.⁷⁵ PCB fluxes calculated from sediment and settling particles averaged 2 to 4 ng cm⁻² a⁻¹ with good agreement between different data sets. Burns *et al.*⁷⁵ estimated residence times based on their measurements of PIT material at 100 m and on fluxes calculated from sediment data. The authors believe that their estimates for PCB fluxes based on settling particles are fairly accurate since they are supported by agreement with fluxes into sediments. Thus, the residence time of PCBs in the upper water column should lie in the range of 2 to 4 years.

The residence times of DDTs and PCBs in the Rijeka Bay, Croatia, were calculated using six mathematical relationships.⁷⁶ As seen from Table III, the residence times for DDTs range from 1.3 years (calculated using the assumptions of Tanabe and Tatsukawa) to 11.5 years (calculated from the sediment data provided in the Burns and Villeneuve relationship and concentrations integrated over 60 m of the water column). For PCBs, residence times range from 1.2 to 9.3 year.

Six species of marine organisms, collected seasonally from the Italian coast of the northern Adriatic Sea over a four-year period (1976–1979), were analyzed for their chlorinated hydrocarbon content.^{79,80} Results indicate that there is an almost uniform distribution of these compounds along the Italian coast of the Adriatic, with the notable exception of the interior of lagoons and areas near the mouths of the Adigo and Po rivers. Levels are similar to or lower than those in related species from other industrial and urban areas of the Mediterranean and other parts of the world, though the Northern Adriatic is often considered a heavily stressed basin. On the basis of the data presented, it seems that the amounts of organochlorine compounds accumulated by the analyzed species were related to their lipid (EOM) content and their trophic level. The arrangement of species according to the tissue level of chlorinated hydrocarbons (*Nephrops* < *Carcinus* > *Mytilus* < *Mullus* = *Engraulis* < *Thunnus*) only in part reflects their lipid content. The ability of mussels to accumulate some lipophilic pollutants, petroleum hydrocarbons and chlorinated hydrocarbons, is highly influenced by their lipid content but the relationship is very complex owing to the different mechanism of accumulation and utilization of lipid reserve in different seasons. Levels of investigated pollutants for anchovies were comparable to

TABLE III

Estimated residence times, RT, of chlorinated hydrocarbon residues in the top 60 m of the Rijeka Bay water column and the complete Bay (modified from Picer, N., 1990)⁷⁶

Calculation method	Range of residence times, RT / years	
	DDTs	PCBs
a)	1.3 to 3.7	1.2 to 2.7
b)	6.7 to 11.5	6.7 to 9.3
c1)	1.1 to 1.7	2.2 to 2.3
c2)	1.0 to 2.1	1.2 to 2.1
d1)	3.8 to 5.1	4.4. to 6.4
d2)	3.6 to 4.8	2.3 to 6.0

a) Calculated using the assumptions of Tanabe and Tatsukawa,⁷⁷

$$RT = \frac{m_{60}}{2.32 \times c_{ss} \times v_{Cprod}}$$

where m_{60} is the mass of chlorinated hydrocarbons present in the water column 1 m² by 60 m depth, c_{ss} is the average concentration of chlorinated hydrocarbons on suspended matter in the surface waters and v_{Cprod} is the rate of primary production of carbon at the surface.

b) Calculated from sediment data given in Burns and Villeneuve⁷⁸ and concentrations integrated over 60 m of the water column:

$$RT = \frac{m_{60}}{F_C}$$

where F_C is the flux of pollutants into sediment per m² and year.

c) Calculated on the basis of relationship:

$$RT = \frac{m_C(\text{Aquat.})}{F_C(\text{Bay})}$$

where $m_C(\text{Aquat.})$ is the mass of pollutants in Aquatorium and $F_C(\text{Bay})$ is the flux of pollutants in the total Rijeka Bay. The mass of pollutants in Aquatorium could be calculated in two ways: c1) from the pollutant mass fraction of fish in the Bay and c2) from that of sestone.

d) Calculated on the basis of relationship:

$$RT = \frac{m_C(\text{Aquat.})}{I_C(\text{Bay})}$$

where $m_C(\text{Aquat.})$ is the mass of pollutants in Aquatorium and $I_C(\text{Bay})$ is the inflow of pollutants into the Rijeka Bay. The mass of pollutants in Aquatorium could be also calculated in two ways: d1) from the pollutant mass fraction of fish in the Bay and d2) from that of sestone.

those found in mullet, though the lipid contents of the two species were very different. Tuna, the biggest predatory fish of the Adriatic, contained the highest concentrations of DDT and PCB while having a lipid content comparable to or lower than mullet. Evidently, the food, the habitat and the physiology of various organisms strongly influence their accumulation capacity.^{79,80}

In the natural environment, highly similar PCBs congener patterns are usually found within each compartment. Between the compartments, however, the patterns often differ significantly, depending on the physico-chemical properties of the individual PCBs, the biokinetic routes (uptake, elimination and metabolism) and the degradation and decomposition kinetics. Two major structural factors determine the environmental fate of PCBs, *viz.* the degree of chlorination and the position of the chlorine substitutes. These factors, together with species characteristics, particularly the differences in basal levels of certain isozymes of cytochrome P-450, from species to species also govern the biotransformation of PCBs. Major components of technical PCB mixtures *e.g.*, PCBs 28, 110, 118, 138, 153 and 180, will almost always be found as major constituents of the total PCB content in abiotic samples. In biota, however, due to the metabolic breakdown, significantly different, but specific congener patterns can be observed for each species. Planar PCBs are highly accumulative in lower organisms. As to the selective accumulation of the planar PCBs and the mono-*ortho* congeners in higher animals, contradictory results have been reported.¹⁷ In contrast to the relatively rapid uptake and release of many other PCB isomers by green-lipped mussels (*Perna viridis* Linnaeus), the non-*ortho* chlorine substituted coplanar PCB congeners exhibited slow uptake and clearance.⁸¹

Examination of chemical transfer from sediments to aquatic organisms indicated large differences in the behavior between PCBs and PCDD/Fs. Biota/sediment accumulation factors for trout averaged 102 among 61 CB isomers, while factors for two 2,3,7,8-substituted PCDD/Fs were below 3 and most were well below 1. Non-2,3,7,8-substituted congeners are also major contributors to Sigma PCDD/F levels in the sediment and biota.⁸²

Spatial variability shows an enrichment of organochlorine compounds (OCs) in a thermohaline front located midway between the Iberian Peninsula and the Balearic Islands. Vertical profiles of OCs in the suspended matter (SPM) show, for the first time, a surface enrichment pattern exhibiting concentration maximum in phyto- and zooplankton zones and declining OC concentrations with depth, except for the nearby sewage disposal sites offshore from Barcelona. Residence times of the SPM were estimated at every depositional area ranging from 1.46 to 8.05 years for PCBs and from 0.46 to 1.32 years for DDTs. The PCB budget in the seawater of the western Mediterranean was computed. The DDT budget was estimated to be *ca.* 179

and 717 kg in the particulate and dissolved phases, respectively. Finally, the input of PCBs through the Gibraltar and the output through Sicilian Straits amounted for 1.5 and 1.3 t per year, respectively. Concurrently, the corresponding input and output for PCBs were 92 and 82 kg per year through Gibraltar and Sicilian Straits, respectively.¹⁰²

LEVELS AND TRENDS

Statistical investigation of chlorinated hydrocarbon levels in many biotic and abiotic samples from the Adriatic Sea shows that standardized coefficients of the kurtosis and skewness are much higher than 2, which means that these data may depart significantly from a normal distribution. Consequently, medians and geometric means should be more appropriate measures of the central tendency of the investigated pollutant data than arithmetic means (averages). However, averages were used in this paper when Adriatic data were compared with data from other marine regions, because, unfortunately, they were the most common statistical parameter reported in the literature.⁸³ Due to non-normal distributions of the elaborated data, it was necessary to use logarithmic values. These values approximated well a normal distribution, which is a prerequisite for the use of parametric statistics.⁸⁴ Thus, the annual means of the natural logarithmic values and their standard errors were compared to study levels and changes of the chlorinated hydrocarbon concentrations or mass fractions within or among the various investigated areas when single data were available.

Water

The concentrations of DDT total and PCBs found by various authors in different seawater samples (film, particulate matter, dissolved phase, and non defined »seawater« samples) collected from various sites in the Mediterranean Sea are summarized in Table IV. Map of the Mediterranean area is presented in Figure 4.

Risebrough *et al.*¹⁰⁰ reported significantly lower concentrations of PCBs in French coastal waters than Elder.⁸⁵ They concluded, on the basis of mass balance calculations that PCBs values in seawater in excess of 1 ng dm^{-3} in both the Atlantic and the Pacific appear to be too high since pentachlorobiphenyls, the dominant PCB present in seawater extracts, had not been produced in sufficient amounts to account for the estimated burden in seawater.

Persistent chlorinated hydrocarbons were analyzed over a two-year period (1977–78) in about 50 water samples collected from the Rijeka Bay coastal waters.^{11,93} Most of the results lie below the analytical sensitivity of

TABLE IV

Concentrations of chlorinated hydrocarbons in surface film (S.F.), seawater (S.W.), seawater-dissolved phase (S.W.D.P.), and particulate matter (P.M.) from the Mediterranean Sea

Area ^a	Matrix	Pollutant	Concentration / ng dm ⁻³			Refs.
			average	min.	max.	
II	S.F.	PCBs	21.6	-3.2	58.3	75, 78
II	S.W.	PCBs	8.5	ND ^b	38	74, 75, 78, 85-88
II	S.W.D.P.	PCBs	0.3	-	-	75
II	P.M.	PCBs	0.7	-	-	75
III	S.W.	PCBs	21.1	0.2	19	74, 89
IV	S.W.	DDTs	12.4	9.0	15.7	74, 89, 90
		PCBs	2.3	0.2	11.6	
IV	S.W.	PCBs	210	50	548	91
VI	S.W.	PCBs	1.8	1.7	1.9	89
VII	S.W.	PCBs	0.9	0.2	1.7	74, 89
VIII	S.W.	DDTs	0.9	0.4	1.5	74, 92
		PCBs	1.5	0.2	2.8	
X	S.W.	PCBs	0.4	0.1	0.8	89
Adriatic	S.F.	DDTs	1.9	ND	25.5	11, 93
		PCBs	51	0.9	597	
Adriatic	S.W.	DDTs	5.1	ND	95	11, 93, 94, 95-99
		PCBs	4.1	ND	17	
Adriatic	P.M.	DDTs	0.6	ND	2.4	94-98
		PCBs	3.3	0.7	9.1	
Adriatic	S.W.D.P.	DDTs	0.5	-	-	94-98
		PCBs	2.0	-	-	

^a See Figure 4.

^b ND, non detected (under detection limit); -, no available data.

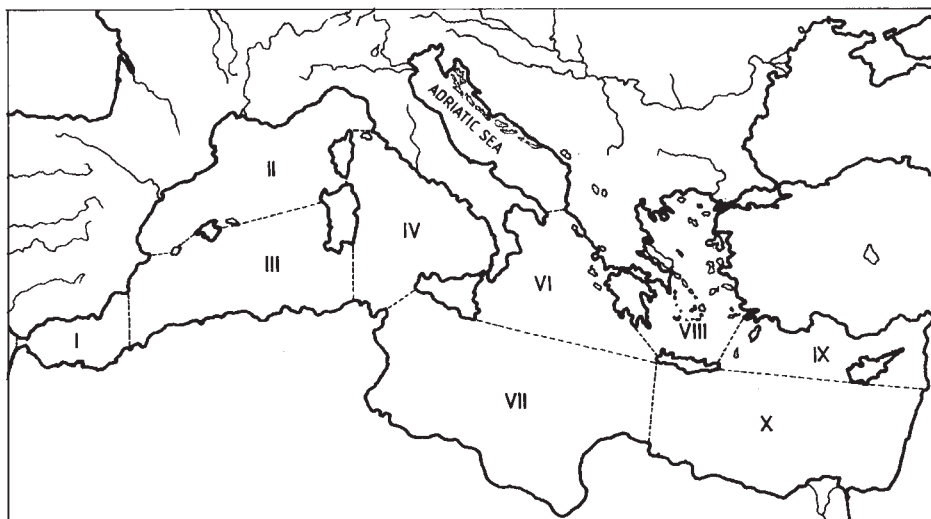


Figure 4. Map of the Mediterranean area (modified from UNEP/FAO/WHO/IAEA).⁴³

the method used (for DDTs 0.05 ng dm^{-3} and for PCBs 0.1 ng dm^{-3}). Only a few samples show traces of chlorinated hydrocarbons. The concentrations of PCBs for all the investigated areas in the Mediterranean Sea and the Rijeka Bay are in a similar range except in the Ligurian Sea. Although there are fewer data for DDTs, the levels are also comparable, except for the Ligurian Sea where the DDTs concentration is significantly higher than in the Rijeka Bay samples.

Slicks are often seen on coastal and open seawater and have been reported to concentrate organic and inorganic pollutants, and marine leptocephali. Larsson *et al.* have estimated the amount of lipids in surface samples to vary between 0.3 and 20 mg m^{-2} .¹⁰¹ Concentration factors are calculated on the basis of water and lipid weight. For coastal waters, it has been assumed that the amount of lipids is 20 mg m^{-2} and 5 mg m^{-2} for open waters. There are no significant differences in concentration factors for the chlorinated hydrocarbons in the open water samples. However, in more polluted coastal water samples, PCBs are more concentrated in the surface film than are DDTs and dieldrin. It could be concluded that although PCBs and DDTs are sorbed preferentially to suspended matter and are more concentrated in surface films than in lower water masses in the water environment, there are some differences between them. It seems that PCB distribution in coastal zones is slightly higher due to sedimentation and evaporation from the surface film than that of DDTs in the Rijeka Bay Aquatorium, as it was previously described for the western Mediterranean.⁶⁶

Individual PCB congeners (IUPAC Nos. 28, 52, 44, 70, 101, 118, 153, 138, 187, 128, 180, and 170), hexachlorocyclohexanes (HCHs) and dichlorodiphenylethanes (DDTs) were determined in 15 samples of suspended particulate matter (SPIM) $> 0.7 \mu\text{m}$ collected in the Catalan Sea and the Gulf of Lions.¹⁰² Furthermore, 6 vertical profiles were sampled at the Ebro and Rhone River mouths, Sicilian and Gibraltar Straits, offshore Barcelona and in the open sea. Finally, 6 dissolved phase samples from the Catalan Sea were taken and analyzed. The highest PCB and DDT concentrations were detected offshore Valencia (26 and 2.8 pg dm^{-3} , respectively). Other sources of pollution were identified at the Ebro transect. Individual chlorobiphenyl (CBs) and *p,p'*-DDE were determined in solution and suspension in surface transects of the open Mediterranean Sea in 1987.¹⁰³ Large volumes of sea water ($1400\text{--}1700 \text{ dm}^3$) were analyzed. Concentrations of CBs were low in solution.

Sediments

Bottom sediments are often the best available medium for long term monitoring of many contaminants in aquatic recipients. Sediment monitoring is carried out by measuring the level of the contaminant in surface sediment samples, often in the upper 0.5–1 cm. This is done at time interval in order to assess the present level of pollution and to detect changes in the flux of that contaminant.¹⁰⁴

Comparison of the mass fraction of chlorinated hydrocarbons in sediment samples obtained from various areas of the Mediterranean Sea and of the mass fraction of these pollutants in sediments collected from the Adriatic is presented in Table V. Comparing the averages of DDT mass fractions in sediments of the whole Adriatic with the averages of levels in the other Mediterranean areas, it can be seen that in six areas of the Mediterranean Sea (II, III, VI, VIII, IX and X) these levels are higher. For PCBs, the mass fractions are higher in five areas of the Mediterranean Sea (I, II, IV, VI and VIII) in comparison with the sediment samples collected from the Adriatic Sea.

Figure 5 and Figure 6 present the levels and the trends of DDTs and PCBs as a natural logarithm of the means and their standard error of mass fraction in sediment samples (dry weight basis) collected from different investigated areas of the eastern Adriatic coastal waters in the period 1976–1990. Sediment samples collected between 1983 and 1990 from the Istrian coastal area, Zadar, Dubrovnik and Montenegrin coastal areas⁴¹ were investigated within the Yugoslav Monitoring Programme, Phase 2. Especially interesting are the extremely high levels of PCBs and DDTs and their dramatic decrease in the Dubrovnik area. This is obviously a result of analytical difficulties at the beginning of monitoring the chlorinated hydrocar-

TABLE V

Mass fractions (w) of chlorinated hydrocarbons in sediments (dry weight) from the Mediterranean Sea

Area ^a	Pollutant	$w_{dw} \times 10^9$			References
		average	min.	max.	
I	DDTs	2.7	0.4	11.0	74, 105
	PCBs	34.6	0.3	323	
II	DDTs	8.2	0.4	200	75, 78, 86–88, 105–111
	PCBs	85.5	0.2	15850	
III	DDTs	11.0	1.2	40.0	74, 105
	PCBs	7.4	0.1	14.0	
IV	DDTs	4.3	0.2	27.0	74, 91, 105, 112, 113
	PCB	102	0.6	3200	
VI	DDTs	10.3	0.1	35.5	89, 105, 112
	PCBs	38.1	0.8	347	
VII	DDTs	0.2	0.1	0.4	105
	PCBs	0.8	0.1	1.1	
VIII	DDTs	128	0.3	1893	89, 105, 114
	PCBs	155	0.6	775	
IX	DDTs	12.0	0.4	29.0	89, 105, 115, 116
	PCBs	1.5	ND ^b	3.0	
X	DDTs	390	1.0	780	89, 105
	PCBs	2.2	0.6	5.1	
The Adriatic Sea	DDTs	6.8	ND	47.8	11, 75, 93, 95, 98, 105, 117–120
	PCBs	24.1	ND	332	
The Adriatic Sea, 1997 ^c	DDTs	3.7	0.2	35.0	121
	PCBs	181	6.0	2203	

^a See Figure 4.

^b ND, not detected (under sensitivity limit).

^c Samples collected during 1997 from the coastal waters of the city of Zadar, Krka estuary near Bilice, Vransko Lake near Biograd, and the Dubrovačka River near Komolac.

bons in samples from the Dubrovnik area. Statistically significant differences were obtained by the one-way analysis of variance of total DDT and PCB mass fractions, depending upon the collection period for chlorinated hydrocarbon mass fraction in sediment samples collected from the Adriatic sea eastern coastal waters during the 1976–1990 period and analyzed by CMR Zagreb.¹¹⁸

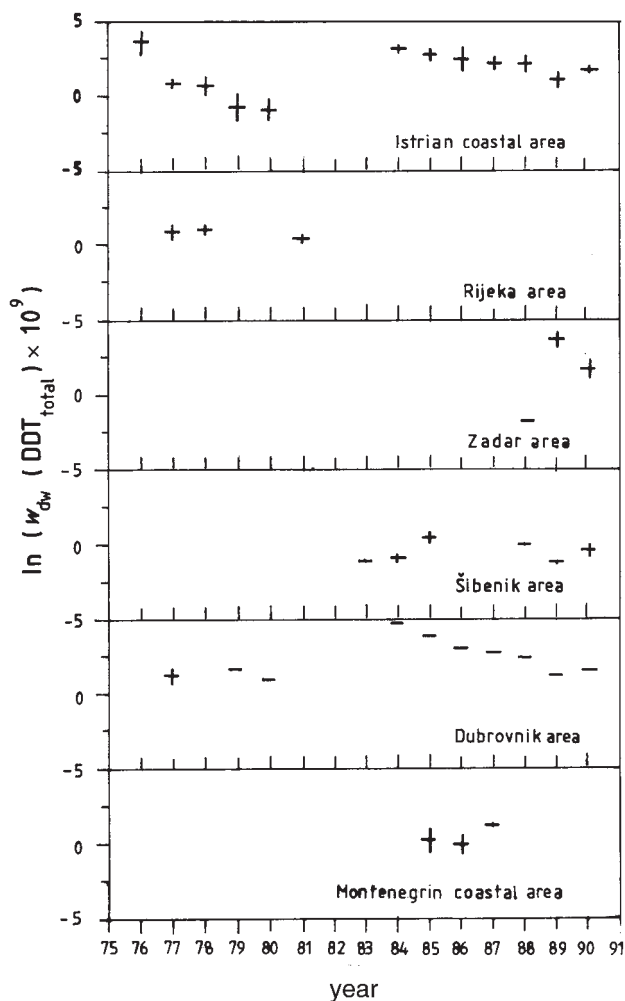


Figure 5. The levels and the trends of DDTs as a natural logarithm of the means and their standard error of mass fraction in sediment samples (dry weight basis) collected from different investigated areas of the eastern Adriatic coastal waters in the period 1976–1990 (modified from UNEP).⁴¹

Although mass fraction data of DDTs and PCBs in sediment samples collected from the open waters of Northern Adriatic have statistically significant differences, levels neither for DDTs nor for PCBs show any statistically significant yearly trend (Figure 7). Comparison of the natural logarithm of the means and their standard error of chlorinated hydrocarbon mass fraction, organic matter and silt content in sediments from the North

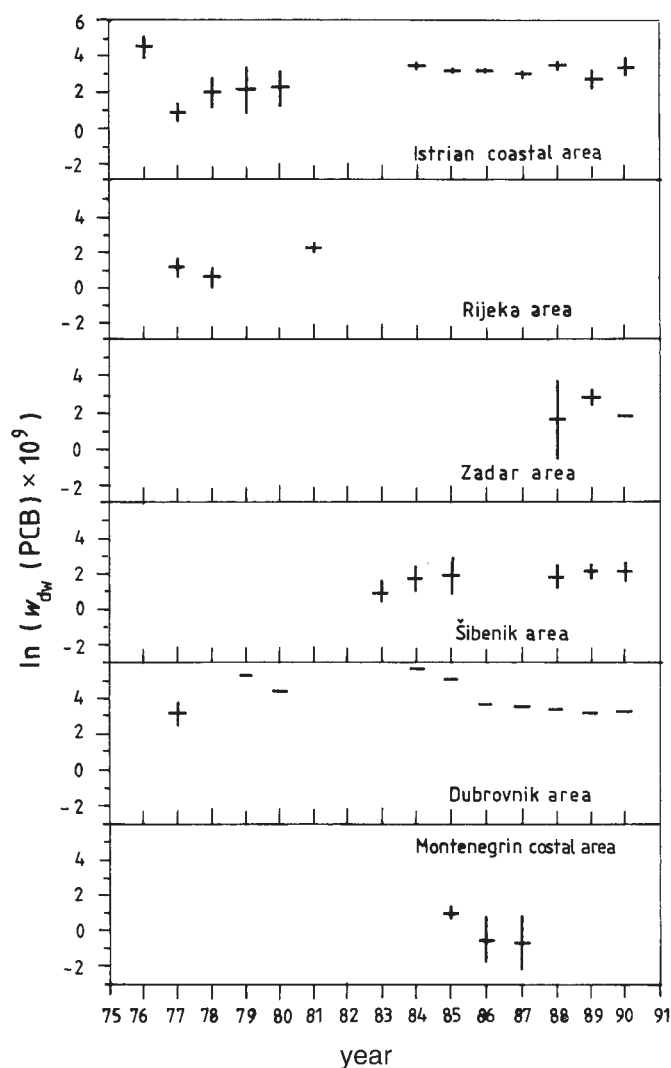


Figure 6. The levels and the trends of PCBs as a natural logarithm of the means and their standard error of mass fraction in sediment samples (dry weight basis) collected from different investigated areas of the eastern Adriatic coastal waters in the period 1976–1990 (modified from UNEP).⁴¹

and Middle Adriatic collected in three areas (west, middle and east) shows that, for both groups of chlorinated hydrocarbon pollutants, the highest levels of pollutants were found in the western part of the Northern Adriatic.⁴¹

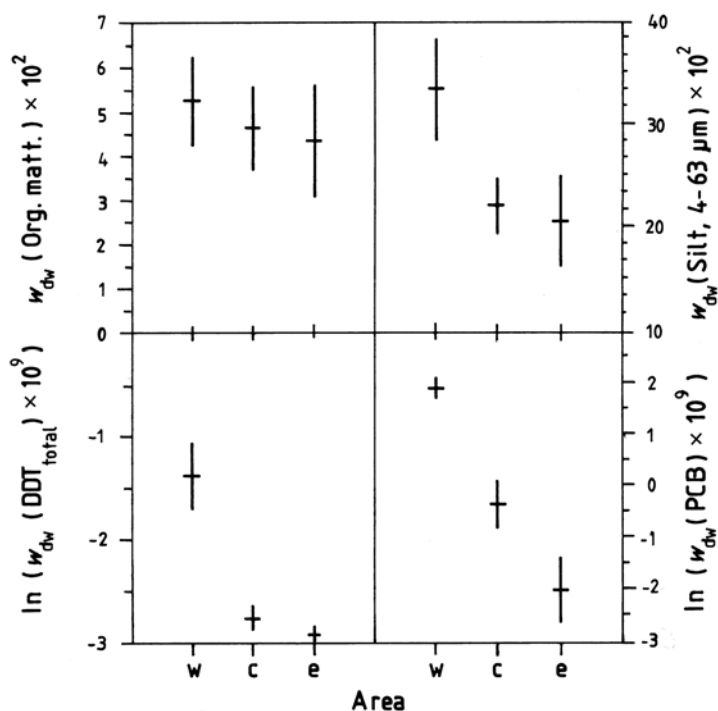


Figure 7. Natural logarithm of the means and their standard error of chlorinated hydrocarbon mass fraction, organic matter and silt (4–63 μm) content in sediment from the northern and central Adriatic for three areas: west, w; middle, m; and east, e (modified from UNEP).⁴¹

The investigation of organic pollutants in the marine environment of the Montenegro Coast of South Adriatic (1989) shows that chlorinated hydrocarbons in sediments were generally very low and not always present.¹²²

Time trend of PCB levels in surface sediments from a hypertrophic, macroalgae populated area of the lagoon of Venice was investigated by Pavoni *et al.*¹²³ The lagoon of Venice is a shallow transitional environment of 549 km^2 with an average depth of 1 m. Water exchange ($(1.6\text{--}5.2) \times 10^8 \text{ m}^3 \text{ d}^{-1}$) occurs with the Adriatic Sea through three entrance channels. (Figure 8). The levels of polychlorinated biphenyls have been determined over a period of 1 year in surface sediments sampled monthly and semi-monthly in the lagoon of Venice. In the lagoon of Venice, PCB contamination has spread mainly from the surroundings of the industrial district of Porto Marghera. A PCB source related to the inflow of fresh waters to the lagoon was also identified by Raccanelli *et al.*¹²⁴ The levels of PCBs in the surface sediments sampled before the growth period of algae in 1985 (13 ppb, dry wt., 10 March)

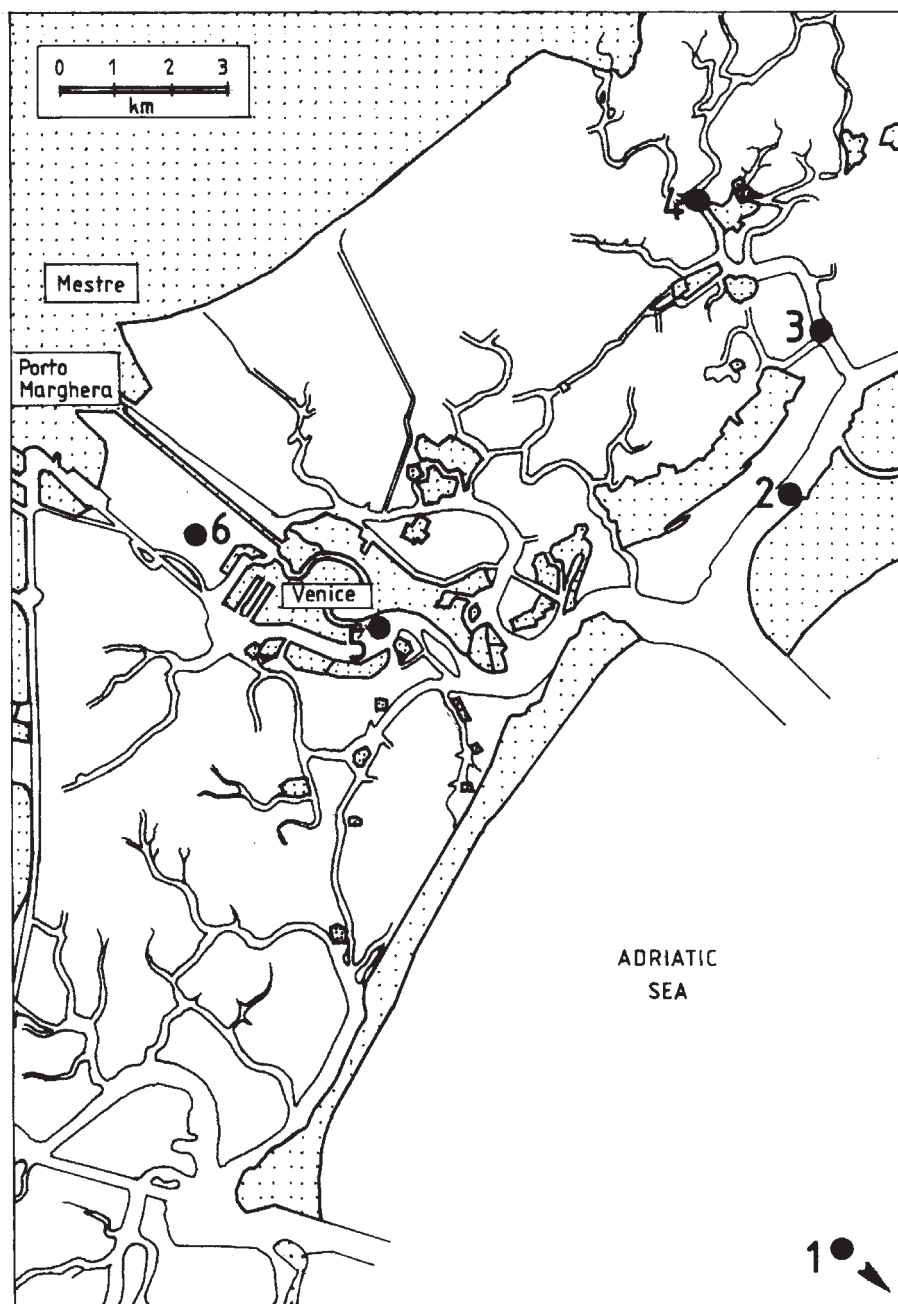


Figure 8. The sampling sites in the Venice Lagoon and North Adriatic Sea. Site 1, reference Platform Site; site 2, Lio Grande; site 3, Crevan; site 4, Torcello; site 5, Salute; site 6, Porto Marghera (modified from Pavoni *et al.*).¹²³

and at the beginning of the growth season in 1986 (12 ppb, 16 April) are slightly lower than the values reported by Donazzolo *et al.*,¹¹⁷ for sediments sampled in 1977 in the lagoon area between the industrial district and the city of Venice (38 ppb). They are consistent with those reported by Pavoni *et al.*:¹²⁵ 19 ppb as an average of the mass fractions for the upper three sections of a core collected in 1982 in the same area, and those reported by Racanelli *et al.*¹¹⁹ During the algae growing season, the PCB level trend is correlated with the organic carbon content of the sediment.

One hundred and fifty five surface sediment samples were collected in six zones of the Gulf of Venice and analyzed for DDTs and PCBs. Mathematical analysis of the data indicated a significant correlation between the chlorinated hydrocarbon content and the percentage of the 63 μm fraction of sediment. There was also a linear relationship between the logarithm of the mass fraction and the percentage of pelite in sediment. A closer examination of the mean values of each zone indicated that three zones are characterized by higher DDT levels, probably because of solid materials transported by the rivers from highly cultivated areas of northern Italy.^{117,125}

Results are reported from experiments on the distribution of organic carbon and organic nitrogen in sediments and resuspended sediments, using undisturbed sediment cores from the Venice lagoon.¹²⁶ The shear stresses applied were equivalent to those which could be produced by wind waves during storms. At all sampling sites, the carbon/nitrogen atomic ratio of resuspended sediment was lower than that of the corresponding underlying sediment. This was attributed to the lower degree of decomposition of organic matter in resuspended sediment. The levels of polychlorinated biphenyls in resuspended sediment at considerable distances from a source of contamination were higher than expected; this might have been due to contributions from animal material.

Surface sediment samples were collected at six locations of the Lagoon of Venice reflecting potential different contamination sources and representative of different hydrological situations.¹²⁷ Analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), linear alkylbenzenes (LABs) and coprostanol were carried out by gas chromatography-mass spectrometry (GC-MS) to assess the influence of various pollution sources: urban, industrial and combustion processes. PAHs, PCBs, coprostanol, and LABs showed the highest levels in the samples collected within the city of Venice (Canal Grande) indicating a very heavy contamination due to combustion sources and to the domestic waste waters directly entering the canals of the city. The highest levels of PCDDs/PCDFs were found in samples collected near the industrial area of Porto Marghera. The

investigation on the PCDDs/PCDFs homologue profiles suggested the presence of two different sources for these pollutants, one due to combustion processes and the other due to the chemical contamination.

A total of 30 NW Mediterranean surficial sediment samples collected in the prodeltas of the Rhone and Ebro Rivers, continental shelf, slope, and deep basin were analyzed for 12 individual polychlorinated biphenyl (PCB) congeners, chlorinated diphenylethane pesticides (2,4'- and 4,4'-DDT and their metabolites), and hexachlorobenzene.¹²⁹ The spatial distribution of the PCB congeners and their levels illustrate the relative contribution to the pollution burden in the NW Mediterranean basin of river inputs, urban sewage disposal, and atmospheric deposition, the latter particularly relevant in the deep basin. Estimates of annual fluxes of these compounds in the NW Mediterranean sediments were from 0.5 to 1580 $\mu\text{g m}^{-2}$ for PCBs (in Clophen A60 equivalents), and from 0.3 to 2060 $\mu\text{g m}^{-2}$ for DDTs (DDT + DDE + DDD). These results account for an accumulation rate in the whole area of 2705 kg per year for PCBs and 2030 kg per year for DDTs. However, the major accumulation of organochlorinated compounds was found to occur in the prodelta areas with an apparent decrease in the Rhone area during the last 15 years, but not in the Ebro, probably reflecting the earlier banning of the use of these compounds in that region.

Plankton and Plants

In Table VI, chlorinated hydrocarbons in plankton and plants from the Mediterranean Sea are compared to the same organisms sampled in the Adriatic. Cattani *et al.*,¹³³ reported levels of DDTs and PCBs found in zooplankton samples collected from two stations in the Italian coastal waters of the northern Adriatic. The levels of PCBs, which were consistently higher than pesticides, show seasonal variations which seem to be correlated with the biomass of *Cladocera* which are more abundant during summer. The results suggest that levels of chlorinated compounds in zooplankton of the northern Adriatic were generally lower than the levels previously reported for this same area.¹³⁶ However, a comparison between the data of mass fractions of pesticides in planktonic organisms is not straightforward since the results can be affected by *e.g.* the determination, such as taxonomic composition of samples and the size of planktonic organisms.

Chlorinated hydrocarbons⁹⁴ (BHC, DDT and metabolites, and PCBs) were determined in sea water, in particulate suspended matter and in net zooplankton samples collected from the area facing the Po River delta during August 1979 and September 1980. As expected, chlorinated hydrocarbon values in the area under consideration are higher than those reported for net zooplankton and waters of the eastern coast of the Adriatic and the open

TABLE VI

Mass fractions of chlorinated hydrocarbons in plankton and plants from the Mediterranean Sea ($w \times 10^9$, fresh weight)

Plankton

Area ^a	Pollutants	$w \times 10^9$			Refs.
		average	min.	max.	
II	DDTs	1.3	ND ^b	2.2	130, 131
	PCBs	55	5.0	180	
IV	DDTs	6.3	0.8	13	132
	PCBs	16.7	2	66	
VI	DDTs	3.4	0.3	61.1	132
	PCBs	4.7	0.6	9.6	
Adriatic	DDTs	4.9	ND	59	76, 93, 94, 96, 133
	PCBs	48.2	ND	453	

Plants

Area ^a	Organisms	Pollutants	$w \times 10^9$			Refs.
			average	min.	max.	
II	Plants (2 species)	DDTs	3.3	ND	25.6	134
		PCBs	20.8	ND	28.8	
VI	Plants (12 species)	DDTs	0.9	0.1	3.9	135
		PCBs	11.7	2.7	39.4	
Adriatic	Plants (2 species)	DDTs	1.6	—	—	95
		PCBs	4.3	—	—	

^a See Figure 4.

^b ND, non detected (under sensitivity limit); —, no available data.

Mediterranean sea. A considerable fraction of chlorinated hydrocarbons is associated with the suspended matter; moreover, this amount increases (total BHC < total DDT < total PCB) with the decrease of their solubility in sea water. Levels of total DDT and total PCB in the particulate matter and in the net zooplankton are similar in terms of dry weight mass fractions, with application factors of 10^4 . On a per volume basis, the absolute quantities of chlorinated hydrocarbons in zooplankton represent only a few percent of these in the particulate mater, due to the different abundance of the two components.⁹⁴

Heavy metals and chlorinated hydrocarbons in the plankton of the North and Middle Adriatic Sea were investigated by Campesan *et al.* The paper reports the results of the analyses of Hg, Cd, Cu, Zn, total DDT, total HCH and total PCB in net plankton collected from the North and Middle Adriatic during ASCOP 0/1, 2 and 3 cruises. The risk of contamination of samples during collection as well as the spatial distribution of these pollutants are discussed; then the levels in the Adriatic are compared with those reported for other areas of the Mediterranean Sea.^{137,138}

Picer *et al.*^{76,93} found that the levels of chlorinated hydrocarbons in plankton samples collected from the Rijeka Bay varied considerably. Frequently, levels at the same station differed by nearly one order of magnitude. In the light of these variations, it is not surprising that it was not possible to detect any influence of local pollution sources in the Rijeka Bay when analyzing plankton samples collected from the »open« waters of the Rijeka Bay.

Mass fractions of PCBs, HCHs and DDTs residues in seaweed of the East Coast of Sicily were investigated during 1977/78 by Amico *et al.*¹³⁵ The residues were determined in thalli of 12 species of marine algae. Different seaweed tends to retain variable amounts of water, so residue levels expressed in terms of dry weight are very important. The highest mass fractions found were in samples from an area (Priolo) intensively polluted by nearby industrial activity. The ratio DDTs/PCBs was consistently lower in algae than in animals from the same area, whereas the opposite applied to the ratio DDTtotal/DDE, while peak patterns of PCBs obtained from seaweed were not comparable in proportion with those from animals, and were characterized by higher intensity peaks of shorter retention time. The observed differences might be explained by assuming that the metabolic breakdown of DDT and PCB is a much slower process in seaweed than in animals. However, it cannot be excluded that a differential intake of contaminants contributes to these differences.

Macroalgae are reported to accumulate both heavy metals and organic contaminants, such as polychlorinated biphenyls. Some nitrophile species, such as *Ulva rigida*, have populated large areas of the Venice lagoon, often accounting for > 90% of species for most of the growing season.¹²³ The PCB contents of Macroalgae were determined in both fresh and old fronds. Five samples of young fronds sampled at the surface and five more samples taken near the bottom were analyzed. The PCB mass fraction in young algae was $(27 \pm 12) \times 10^9$ dry wt. and those in old algae $(121 \pm 4) \times 10^9$ dry wt. PCBs levels in older and decomposing algae were therefore ≈ 4.5 times higher than in new fronds.¹²³

Shellfish and Crabs

Many organic pollutants occur in marine waters at concentrations of ng dm^{-3} or less. Methods for the direct analysis of such concentrations in seawater are being developed but the time and expense of handling the large volumes of seawater required prohibit routine use of water analyses in many monitoring programs. Thereafter, several species have been suggested as possible sentinel organisms based on their ability to take up and eliminate a particular set of compounds. Bivalves have proved to be promising candidates since they actively concentrate several classes of pollutants and are attached to filterfeeders.¹³⁹ Since the late 1960s, scientists have been using bivalve filter-feeding mollusks to monitor selected chemical contaminants in coastal marine waters and an extensive »mussel watch« literature has developed from that work.¹⁴⁰

A bimonthly survey was carried out to measure existing levels of some chlorinated hydrocarbons in mussels of Laguna Veneta. The distribution of chlorinated pesticides was quite uniform; significant differences in the distribution of PCBs were observed for samples collected inside the Laguna, indicating the presence of local inputs.¹⁴¹ The overall data, tested by the regression analysis, showed no significant correlation between the residue levels and fat content, while positive correlations were found during summer. This finding suggests that variation in the mussels lipid cycle may be responsible for some variations in the residue levels during the optimal growing conditions and active reproductive period, when the ingestion of food and spawning are relevant factors, affecting the accumulation and removal of lipid and lipophilic pollutants. During winter, the relationships fail, indicating probably a more complex mechanism for accumulation of pollutants and lipids; in fact, the uptake of pollutants from food may be low or comparable with other routes, such as the uptake directly from water and by ingestion of inorganic particulate matter. Furthermore, the build-up of lipid reserves in the eggs may be due to the conversion of prestored glycogen rather than to the assimilation of food.

A comparison of the mass fraction of chlorinated hydrocarbons in mussel samples obtained from various areas of the Mediterranean Sea and of the mass fraction of these pollutants in mussels collected from the Adriatic⁴¹ is presented in Table VII. When comparing the most recent data on these levels obtained for each area with the data obtained during the Yugoslav Monitoring Program, Phase 2, it can be noticed that for the levels recorded DDTs and PCBs during the Yugoslav Monitoring Program are much lower.⁴¹ Also, as regards the mussel data obtained from the analysis of samples collected from the Adriatic Sea in the period between 1976 and 1980, the Yugoslav monitoring data are lower for DDTs about 50% and even more (about four

TABLE VII

Mass fractions of chlorinated hydrocarbons in mussels from the Mediterranean Sea ($w \times 10^9$, fresh weight)

Area ^a	Period of investig.	DDTs		PCBs		Refs.
		$w \times 10^9$		$w \times 10^9$		
		average	range	average	range	
II	1970/74	150.2 (92) ^b	10.0–900.0	395.4 (105)	33.1–2073	100, 111, 141, 142
II	1976/79	25.9 (15)	1.5–46.0	126.1 (15)	10.9–233.0	88, 106, 144–146
II	1979/82	20.5 (34)	4.6–55.4	92.7 (17)	9.1–327.3	85, 148
IV	1978/81	34.7	9.0–57.3	96.4	20.0–172.7	146, 149
VI	1977/78	33.1 (4)	9.0–35.6	78.0 (4)	42.0–100.9	135, 146
VIII	1975/79	23.9 (96)	–	383.4 (96)	–	150
Adriatic	1973	34363 (7)	–	–	–	136
Adriatic	1973/74	98.7 (67)	ND ^c –506.9	153.9 (67)	ND–390.1	76, 83, 146, 151, 152
Adriatic	1976/80	12.9 (140)	ND–301.1	82.5 (77)	ND–1586	76, 83, 146, 151, 152
Adriatic	1983/90	8.7 (108)	ND–41.0	21.2 (107)	ND–68.0	41, 76, 83
The Adriatic Sea	1997 ^d	7.5 (15)	1.5–45.0	356 (15)	12.5–1510	121

^a See Figure 4.

^b Number of samples in brackets.

^c ND, not detected (under sensitivity limit).

^d Samples collected during 1997 from the coastal waters of the city of Zadar, Krka estuary near Bilice, Vransko Lake near Biograd, and the Dubrovačka River near Komolac.

times) for PCBs. Figure 9 and Figure 10 present the levels and the trends of DDTs and PCBs as a natural logarithm of the means and their standard error of mass fraction in mussels (wet weight basis) collected from different investigated areas of the eastern Adriatic coastal waters in the 1976–1990 period.⁴¹

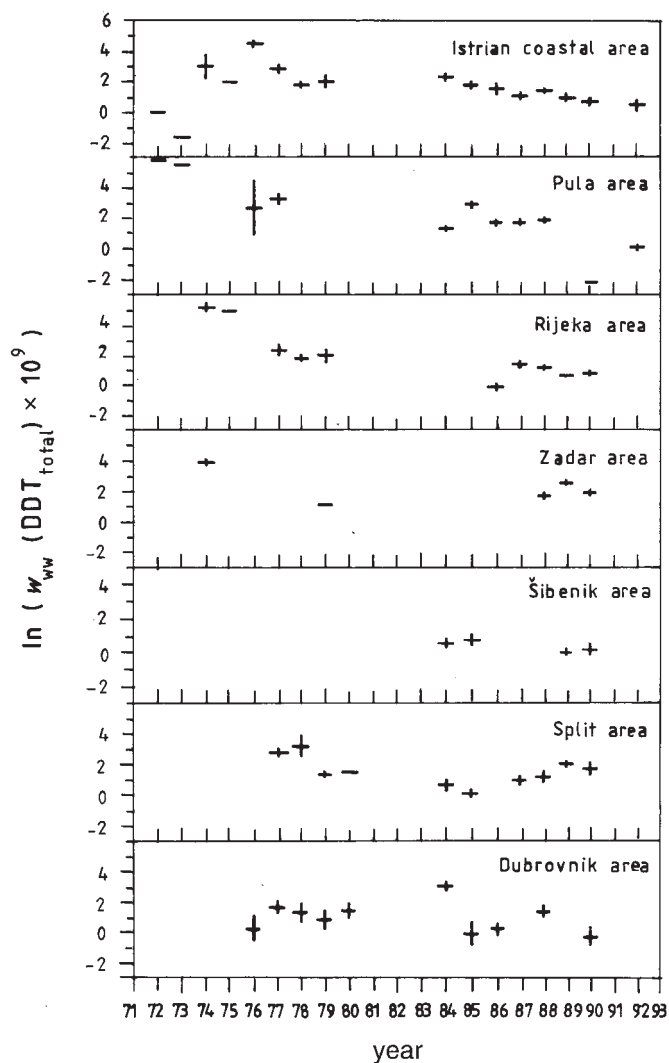


Figure 9. The levels and trends of DDTs as a natural logarithm of the means and their standard error of mass fraction in mussel samples (wet weight basis) collected from different investigated areas of the eastern Adriatic coastal waters in the period 1974–1990 (modified from UNEP).⁴¹

Although several major north Italian rivers discharge into the North Adriatic, mussel samples from Istrian coastal waters did not have significantly higher levels of DDTs and PCBs than did other waters. Chlorinated hydrocarbon levels often differ dramatically in samples collected at stations

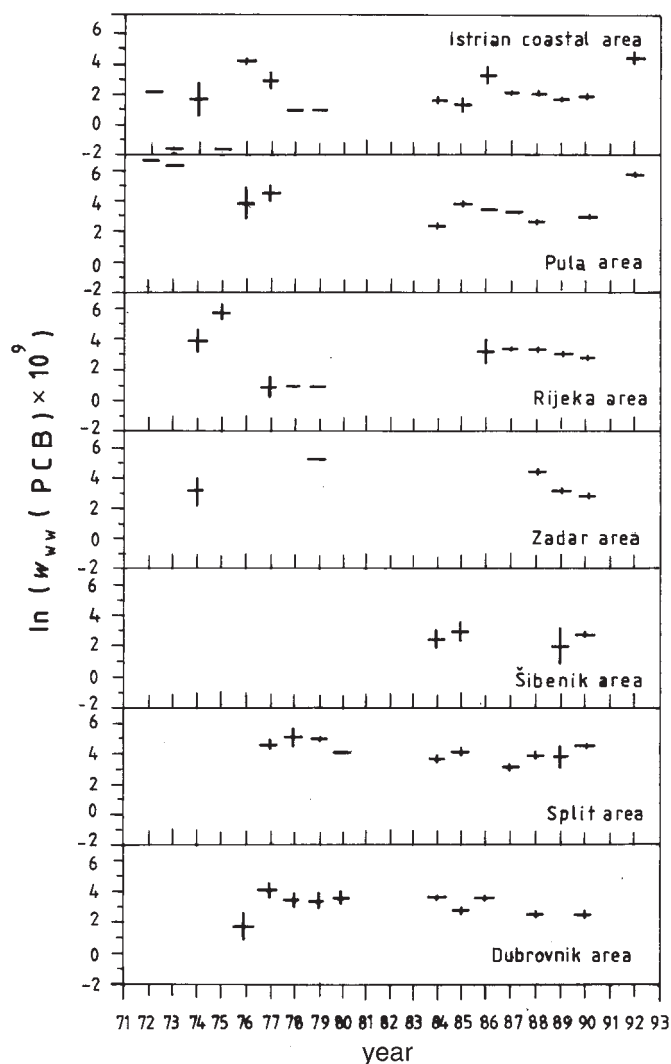


Figure 10. The levels and trends of PCBs as a natural logarithm of the means and their standard error of mass fraction in mussel samples (wet weight basis) collected from different investigated areas from eastern Adriatic coastal waters in the period 1974–1990 (modified from UNEP).⁴¹

which are close together, possibly because the first station water had been contaminated with waste waters and that of the second station had not. Evidently, urban wastewaters even from relatively small settlements contribute significantly to the local contamination of Adriatic waters with chlo-

minated hydrocarbons.¹⁵² Levels of PCBs were significantly higher than those of the DDT group in the samples of mussels collected in the vicinity of the industrial pollution sources of the Rijeka Bay. In the samples collected away from industrial sources of pollution, levels of DDTs were higher than PCB levels. The level of contamination by persistent chlorinated pesticides in mussels throughout the coastal zone of Rijeka Bay appears to be the same. This was somewhat unexpected because it is well known that urban wastewaters are relatively rich in persistent chlorinated insecticides. A possible explanation could be the recent higher use of DDT and its analogues for pest control in agriculture and forestry, because the coastal zone is a typical karstic region and consequently, once applied, pesticides are likely to drain into the Rijeka Bay very quickly.^{76,83}

In the marine environment of the Montenegro coast of the South Adriatic, the contents of DDTs and PCBs are as follows: DDE, 8.2 to 14.4; DDD, 0.3–0.7; DDT, 2.8–3.6; PCB, 0.01 ppb.¹²² The presence of chlorinated hydrocarbons was established in the shellfish tissues of striped venus (*Chamelea gallina*) in Neretva Estuary. Levels of DDT (dry weight) were up to 10 ppb. The values recorded for DDD were exceptionally high: 1050 ppb (dry weight).¹⁵³

The bioaccumulation potential of three highly toxic coplanar PCB isomers (3,3',4,4'-tetrachlorobiphenyl, T4CB; 3,3',4,4',5-pentachlorobiphenyl, P5CB; and 3,3',4,4',5,5'-hexachlorobiphenyl, H6CB) was investigated using green lipped-mussels (*Perna viridis* Linnaeus) as a bioindicator, in a transplantation experiment at two locations in marine waters. In contrast to the relatively rapid uptake and release of many other PCB isomers, the non-*ortho* chlorine substituted coplanar PCB congeners exhibited slow uptake and clearance. The kinetic parameters of coplanar PCBs based on lipid weight-related data, and the degree of bioaccumulation based on the proportion of coplanar PCBs in total PCBs in mussels, clearly indicate that coplanar PCBs are highly bioaccumulative in lower organisms. On the assumption that mussels are unlikely to be particularly unusual with respect to their bioaccumulation of coplanar PCBs, it appears most likely that these highly toxic and persistent PCB congeners are concentrated in all aquatic organisms, and may reach higher consumers (including humans) in quantities of toxicological concern.³⁷

Investigation of the uptake and depuration of planar PCB congeners by the American Oyster (*Crassostrea virginica*) shows that two of the most toxic planar PCB congeners (77 and 126) were bioconcentrated by transplanted oysters during a 7-week exposure period. Congener 77 attained an equilibrium concentration in a shorter period of time than congener 126. When contaminated oysters were transplanted back into the clean marine

area, they significantly depurated both planar PCB congener. However, the estimated depuration half-lives were significantly longer than those corresponding to different PCBs within the same homolog groups. Because of their potential toxicity, this persistency of highly toxic planar congeners is of significant importance in environmental studies. These congeners can be considerably bioconcentrated, and retained, by bivalves and constitute a potential health hazard for higher consumers, including human beings.¹⁵⁴

A comparison of the levels of chlorinated hydrocarbons in crustacean samples obtained from various areas of the Mediterranean Sea and in samples collected from the Adriatic⁴³ is presented in Table VIII. As seen, the highest PCB levels were observed in the Adriatic and the highest DDT levels in crustaceans off the Eastern Mediterranean coast of Turkey.

Carcinus mediterraneus and *Nephrops norvegicus* were collected seasonally from the Italian coast of the northern Adriatic Sea (off Porto Garibaldi and Cesenatico) over a four-year period (1976–1979) and were analyzed for their chlorinated hydrocarbon content. The overall data on chlorinated hydrocarbons show that PCB residues predominate in all species at all stations regardless of the season.¹⁵¹

TABLE VIII
Mass fractions of chlorinated hydrocarbons in crustaceans from the
Mediterranean Sea ($w \times 10^9$, fresh weight)

Area ^a	Organisms	DDTs		PCBs		Refs.
		$w \times 10^9$		$w \times 10^9$		
		average	range	average	range	
II	Two species	6.5	1.2–13.0	71	21–203	88, 144–147
IV	<i>Nephrops Norvegicus</i>	3.3	0.2–16	9	2.9–23.3 –	135, 146, 149
VI	<i>Nephrops Norvegicus</i>	1.2	0.9–1.6	4.9	5.4	135
IX	<i>Parapaneus kerathurus</i>	78.9	8.9–161	ND ^b		15
Adriatic	Six species	8.8	ND–30.2	110	ND–796	95, 146, 151, 155, 156

^a See Figure 4.

^b ND, not detected (under sensitivity limit).

Fishes

Data on levels of DDT and its derivatives, and PCBs found by various authors in fishes collected from the Mediterranean Sea are summarized in Table IX.

Residues of lindane, dieldrin, DDT and its metabolites and PCBs found in fish captured in the Po Delta during 1972 were reported by Viviani *et al.*¹⁶¹ In *Gobius paganellus* chlorinated hydrocarbons were always less than 1 ppm (fresh weight) whereas higher levels (up to 4 ppm) of DDT and its metabolites, and 12 ppm of PCB were found in the liver. The authors claimed that no particular accumulation of the investigated chlorinated hydrocarbons occurs in fish in the Po Delta.¹⁶¹

Viviani *et al.* investigated the presence of residues of DDT, its metabolites and PCBs in muscles and Crisetig *et al.* in ripe female gonads of the North Adriatic *Sardina pilcardus*, *Engraulis encrasicolus* and *Clupea sprattus*. The values of the residues found in the gonads during corresponding periods of »gonadic activity« were rather low, even if considered all together (0.558 ppm in sardine, 0.184 in anchovies and 0.278 in sprats, and were well below the levels found to cause a deleterious effect on trout reproduction: 4 to 74 ppm).^{160,162}

Fossato and Craboledda investigated the distribution of chlorinated hydrocarbons in fish from the Italian coast of the northern Adriatic Sea. The sequence of species according to tissue level of chlorinated hydrocarbons (*Nephrops*, *Carcinus*, *Mytilus*, *Mullus*, *Engraulis*, and *Thunnus*) only partly reflects their lipid content. Levels in anchovies were comparable to those found in mullet, although the lipid contents of the two species were very different. Tuna, the biggest predatory fish of the Adriatic, contained the highest levels of DDT and PCB while having a lipid content comparable to or lower than mullet.¹⁵¹ Of the several species studied, *Engraulis encrasicolus* sampled off Porto Garibaldi and Cesenatico is only one for which comparison over a long period can be made for the area under consideration. The data in Table X show that chlorinated hydrocarbon levels in anchovy sampled during the period from November 1976 to June 1979 were significantly lower than those observed in the same species between 1968 and 1972.⁵⁴

The level of chlorinated hydrocarbons was determined in several fish species (*Gobius sp.*, *Mullus barbatus*, *Diplodus annularis*, *Oblada melanura*, and *Merluccius merluccius*) collected from three areas in the eastern coastal waters of the middle and north Adriatic Sea. Average wet-weight mass fractions of DDTs and PCBs in fish sampled from the three areas were: Istrian coast, 124 and 144 ppb; Rijeka Bay 37 and 82 ppb; Lošinj Island, 166 and 157 ppb, respectively. Dieldrin levels were in the low ppb

TABLE IX
Mass fractions of chlorinated hydrocarbons in the Mediterranean fish ($w \times 10^9$, fresh weight)

Area ^a	Fish species	DDTs		PCBs		References
		$w \times 10^9$		$w \times 10^9$		
		average	range	average	range	
II	<i>Mullus barbatus</i>	68.6	3.0–133.2	556.7	70.3–1618.2	88, 144, 145, 146
	<i>Engraulis encrasicolus</i>	27.4	11.0–48.2	167.1	22.5–330.0	144, 145, 146, 147
	5 various species	234	1–2048	1756	39–11356	88, 108, 143–147
IV	<i>Mullus barbatus</i>	53.1	12.0–86.1	144.2	15.5–373.1	135, 146, 148
	<i>Engraulis encrasicolus</i>	37.3	11.1–73.4	1325.6	19.8–232.3	135, 146, 149
	<i>Thynnus thynnus</i>	37.0	22.5–51.3	40.0	35.5–44.5	135
VI	<i>Mullus barbatus</i>	19.0	4–38	27	22–224	135, 146
	<i>Engraulis encrasicolus</i>	36	11.3–82.8	59	9–177	
	<i>Thynnus thynnus</i>	37	–	40	–	135
VIII	<i>Mullus barbatus</i>	76	4–400	432	14–1613	150, 157, 158
	<i>Thynnus thynnus</i>	1239	–	2613	–	150
	<i>Merluccius merluccius</i>	43	–	510	–	
IX	<i>Mullus barbatus</i>	175	11–379	1.4	ND ^b –2	115, 116
	<i>Upeneus moluccensis</i>	74	27–84	2	–	
X	<i>Mullus barbatus</i>	29	3–83	60	ND–284	159
	Various fishes (3)	25	ND–106	120	ND–800	
Adriatic	<i>Mullus barbatus</i>	31.2	ND–164.2	89.1	ND–188.4	76, 146, 150, 151, 155
	<i>Engraulis encrasicolus</i>	52.9	3.8–102.5	155.6	10.1–240.7	76, 136, 146, 147, 150, 151, 155, 160–162
	Various fishes (27 species)	149	ND–569	209	ND–2650	76, 136, 146, 147, 150, 151, 155, 160–163
The Adriatic Sea, 1997 ^c	Various benthic and epibenthic fishes (7 species)	5.4	0.6–36.0	631	36–4004	121

^a See Figure 4; ^b ND, not detected (under sensitivity limit); ^c Samples collected during 1997 from the coastal waters of the city of Zadar, Krka estuary near Bilice, Vransko Lake near Biograd, and the Dubrovačka River near Komolac.

TABLE X

Temporal comparison of chlorinated hydrocarbon levels ($w \times 10^9$, wet weight; means \pm SD) in *Engraulis encrasicolus* sampled off Porto Garibaldi and Cesenatico

Sampling period	n^a	$w_{ww} \times 10^9$, means \pm SD		Refs.
		DDTs	PCBs	
Nov. 1967 – Sept. 1968			257 \pm 102	164
Jan. 1970 – Nov. 1970	6	280 \pm 116	547 \pm 280	160
Nov. 1972	1	80	370	161
Nov. 1976 – June 1979	16	65 \pm 37	155 \pm 43	151

^a n , number of samples.

range. Statistical analysis of the data showed that the only levels that differed significantly per areas were those of DDTs in samples from the Rijeka Bay *versus* those from the Lošinj area and in samples from the Istrian coast *versus* those from the Rijeka area. The differences in PCB mass fractions were not significant.¹⁵² Revelante and Gilmartin¹⁶³ studied the distribution of chlorinated pesticides and PCBs in the muscle, digestive tract, liver and gonads of several pelagic (6 species) and benthic (11 species) fish from the northern Adriatic Sea. The distribution of some chlorinated pesticides and PCBs was also investigated by Dujmov *et al.*¹²¹ in fishes of the Middle Adriatic and by Kljajić *et al.*¹⁶⁵ and Viličić *et al.*¹⁵⁶ in fishes of the South Adriatic. Chlorinated hydrocarbons in fish (*Mullus barbatus*) in the marine environment of the Montenegro coast in South Adriatic varied – DDE: 0.01 to 4.95, DDD from 0.01 to 0.84; DDT from 4.17 to 15.14 and PCBs from 0.01 to 297.3 ppb.¹²²

Polychlorinated biphenyls and organochlorinated pesticides were extracted from samples of eel muscle (*Anguilla anguilla* L.) caught in the Po Delta and determined by fused silica capillary gas chromatography/mass spectrometry.¹⁶⁶ The main compounds identified were polychlorinated biphenyls, HCB, *p,p'*-DDT and its metabolites, *p,p'*-DDE and *p,p'*-DDD. PCB and DDT levels were higher in eels captured in spring than in those fished in autumn and were correlated with fat values in muscle tissue. Mean PCB levels were 265 \pm 9 and 211 \pm 6.9 $\mu\text{g kg}^{-1}$ wet weight, and those of DDT compounds 18.45 \pm 12.7 and 15.76 \pm 10.6 $\mu\text{g kg}^{-1}$ wet weight, respectively. They were also higher than those determined in other species of fish captured in the same body of water, although the data indicate that there is probably no real health risk from irregular consumption of eel containing these xenobiotic levels.

Taking into account the location of destroyed Zadar and Dubrovnik Electrical Transformer Stations that were encompassed by warfare in 1991/1995, there is some speculation regarding the potential hazard from organohalogenated toxicants to the sea around the Zadar and Dubrovnik areas. In 1997 benthic and epibenthic fish samples were collected and analyzed from Zadar and Dubrovnik areas at six stations. The levels of pollutants in the fish samples ranged from < 0.5 to 353 ppb (before the war) and from < 0.1 to 35.8 ppb (after the war) for DDTs, from < 0.5 to 311 ppb (before the war) and from < 74 to 4004 ppb (after the war) for PCBs wet weight. Figure 11 presents a scatter plot of the logarithmic values of the DDTs and PCBs levels in the fish samples collected from the coastal waters of the Zadar and Dubrovnik areas in comparison with the collection year. In the figure, linear regression line and two pairs of dotted lines representing the 95% confidence and prediction limits are estimated. As seen, a significant negative yearly trend for DDTs levels is obtained. In the case of PCBs, a significant positive yearly trend is obtained.

The bioaccumulation of organochlorinated contaminants (DDTs, PCBs and HCB) in three representative fish species from the Ebro Delta (western Mediterranean) was studied.¹⁶⁷ The species, red mullet (*Mullus barbatus*), sea mullet (*Mugil cephalus*) and sea bass (*Dicentrarchus labrax*), were selected for their characteristic habitats and feeding behaviours to investigate their potential as bioindicators in pollution monitoring studies. Higher levels of PCBs and DDTs were generally found in red mullet and could be related to the higher lipid content of this species. Red mullet and sea bass exhibited a similar distribution pattern of these pollutants, whereas DDTs and HCB (hexachlorobenzene) were relatively more abundant in sea mullet, probably as a result of a direct uptake from the water lagoons from where the latter were collected and where these pollutants were in higher levels. A decrease in levels with size (age) was generally observed in red mullet and sea bass, though less clearly in sea mullet. This decrease was more pronounced for DDTs, probably owing to metabolic transformations. However, when data were normalized to lipid content, evidence for a positive uptake by sea mullet was obtained, probably relating to the higher growth rate of this species. These results indicate that the accumulation of organochlorine compounds in coastal fish from the same area depends on the lipid content, habitat, dietary intake, growth rate and the metabolism of each species. Although these fish can be used for pollution monitoring, the subsequent variability of pollutant body burdens that are influenced by these factor, precludes the extrapolation of data from one species to another.

Mass fractions of PCBs, DDTs, HCHs, HCB, aldrin, dieldrin, chlordanes, heptachlor, and heptachlor epoxide were determined in cod-liver oil samples

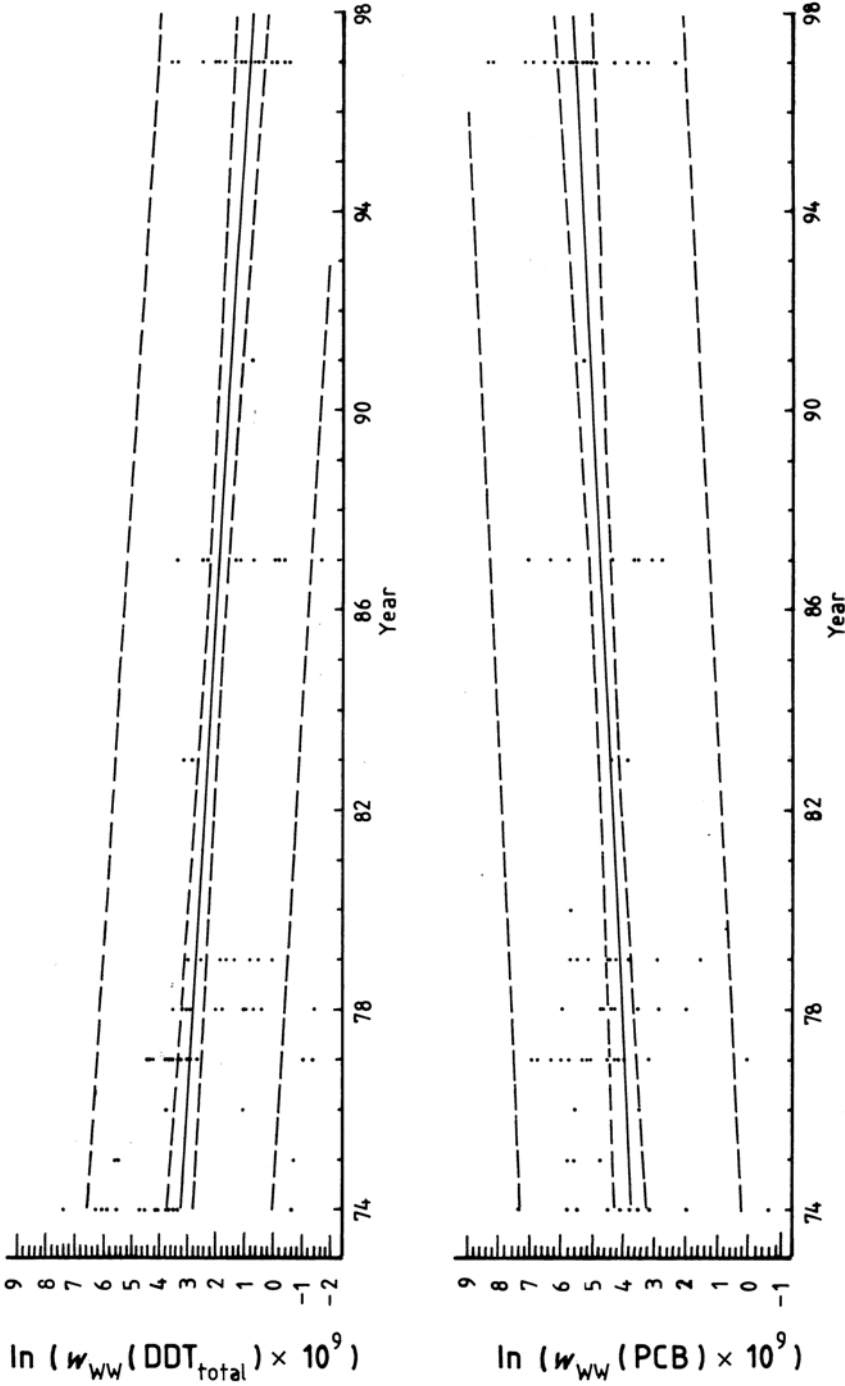


Figure 11. A scatter plot of the logarithmic values of the total DDT and PCB levels in fish samples in comparison with the collection year. In addition, the estimated linear regression line and two pairs of dotted lines representing the 95% confidence and prediction limit are presented.

collected from the southern part of the Baltic proper during 1971–1989 for the purpose of understanding the long-term changes in residue levels and the present status of contamination.¹⁶⁸ There has been a rapid decline in DDT levels from 1974 until the present. PCBs, HCB, aldrin, and dieldrin tended to decrease at a very slow rate while HCHs showed a steady state in their time trends.

The levels of organochlorines in tropical fish were lower than those in fish of the temperate regions.¹⁶⁹ This is different from the patterns observed for air and water in which higher levels occur in tropical latitudes compared to mid-latitudes.

Birds and Other Organisms

Residues of lindane, dieldrin, *p,p'*-DDD and PCB found in birds captured in the Po River delta during 1972 were reported by Viviani *et al.*¹⁶¹ The sea-gull (*Larus ridibundus*) showed the highest levels of DDT and its metabolites (4 ppm in the muscle and liver) whereas the common tern (*Sterna hirundo*) had the highest level of PCB (7.9 ppm in the breast muscle and 8.6 in the liver). By comparison with the literature data the authors considered birds in the Po delta were not particularly contaminated by the organochlorine compounds investigated.

Eggs of the following species from the Adriatic were analyzed over the period 1980/81: little egret, night heron, stilt, coot, avocet, black-headed gull, herring gull, slenderbilled gull, gull-billed tern, common tern and little tern from three areas along the Italian shore.¹⁷⁰ Authors found low levels of most of the analyzed chlorinated hydrocarbons compared with other marine areas of the world. However, the levels of PCB in the eggs of all species but avocet, stilt and coot, were quite high in all sampling areas suggesting a widespread polychlorinated biphenyl contamination.

Fassola *et al.* report on organochlorine pesticide and PCBs levels in eggs of the little egret, *Egretta garzetta*, and the black-crowned night-heron, *Nycticorax nycticorax*, collected in 1993–1994 from heronries near Pavia, northern Italy.¹⁷¹ Organochlorine pesticide and PCB residues were lower than those commonly associated with mortality and reduced reproductive success. As population levels of the species studied are not declining, these contaminants appear to have no significant adverse effect on reproduction in the heronries studied. DDE levels have decreased markedly in heron eggs since 1978.

Relevante and Gilmartin¹⁶³ investigated the distribution of chlorinated hydrocarbons in several samples of *Sepia officinalis* and *Loligo vulgaris*. Levels of DDT total ranged from 1 to 58 ppb wet weight but PCBs were

found lower. For an evaluation of the extent of pollution in the Rijeka Bay, Croatia, by chlorinated hydrocarbons an investigation of their levels in sediments and the most abundant benthic organisms (*Asteroidea* and *Holothuroidea* species) was carried out.¹⁷³ Samples were collected at several stations in October 1981. The levels of DDTs and PCBs in *Asteroidea* species were from 0.5 to 46.0 ppb for DDTs and from 2.5 to 435 ppb for PCBs (wet weight). For the PCBs in *Holothuroidea* species, the values ranged from 4.4 to 37.2 ppb and for DDTs from 0.9 to 48.5 ppb. The relatively low bioaccumulation of PCBs and DDTs from sediments in the Rijeka Bay by the *Asteroidea* and *Holothuroidea* species is reassuring because of the problem of dredging and ocean dumping of sediments polluted with persistent chlorinated hydrocarbons. There is scarce or almost no information, however, on the extent to which the species will contribute to chlorinated insecticides and PCB accumulation in their predators.

Mammals

PCB levels and total lipid content were determined in the blubber and liver of striped dolphins affected by the 1990 morbillivirus epizootic in the Mediterranean Sea,¹⁷³ and in the blubber of striped dolphins from the same area sampled with a biopsy dart in 1987–1989 and 1991. PCB levels were found to be significantly higher in the individuals that succumbed to the epizootic than in the 'healthy' population sampled before or after the event. Although recent mobilization of lipid reserves was found to have occurred in some of the diseased dolphins, this had little effect on their PCB blubber levels and cannot explain the observed difference from the healthy individuals. Three hypotheses are put forward to explain the apparent link between high PCB levels and mortality caused by the epizootic: (i) depressed immunocompetence caused by PCBs leading to an increase in individual susceptibility to the morbillivirus infection, (ii) mobilization of fat reserves leading to increased PCB levels in blood which, in turn, may produce a liver lesion capable of increasing the individual's susceptibility to the morbillivirus infection, and (iii) previous existence of an unspecific hepatic lesion producing impairment of the liver function which, in turn, could lead to an increase both in tissue PCB levels and in individual susceptibility to the morbillivirus infection.

Levels of chlorinated pesticides and polychlorinated biphenyls (PCB) have been determined in tissues and organs of *Stenella coeruleoalba* dolphins beached along the Adriatic and Ionian coasts of Apulia – Southern Italy.¹⁷⁴ The results obtained confirm that in Mediterranean dolphins the accumulation of contaminants is higher than in similar species living in the Atlantic. Therefore, cetaceans can be considered "organisms indicating pol-

lution". Accumulation is influenced by factors such as diet, age and sex. Reproduction plays a fundamental role in the elimination of toxic compounds in females. No correlation between contamination and death has been found; however, it is clear that pollutants at sub-lethal doses have neurotoxic effects, increase stress and alter immune defenses, leaving the organism at a greater risk from disease.

Levels of HCB, DDTs and PCBs in the tissues and organs of cetaceans (*Stenella coeruleoalba*, *Tursiops truncatus*, *Balaenoptera physalus*, *Stenobredanensis*, *Grampus griseus* and *Globicephala melaena*) stranded along the Italian coasts in the period 1987–1993 are reported.¹⁷⁵ The values are compared between species and between specimens of the same species (Figure 12). Chlorinated hydrocarbon levels were found to increase in relation to the quantity and type of lipids in each tissue and organ. Differences in accumulation encountered in the different species are principally due to different feeding habitats. Remarkable differences found between males and females of each species confirm that during gestation and lactation, females undergo disintoxication by passing much of their total burden of CHs to their young.

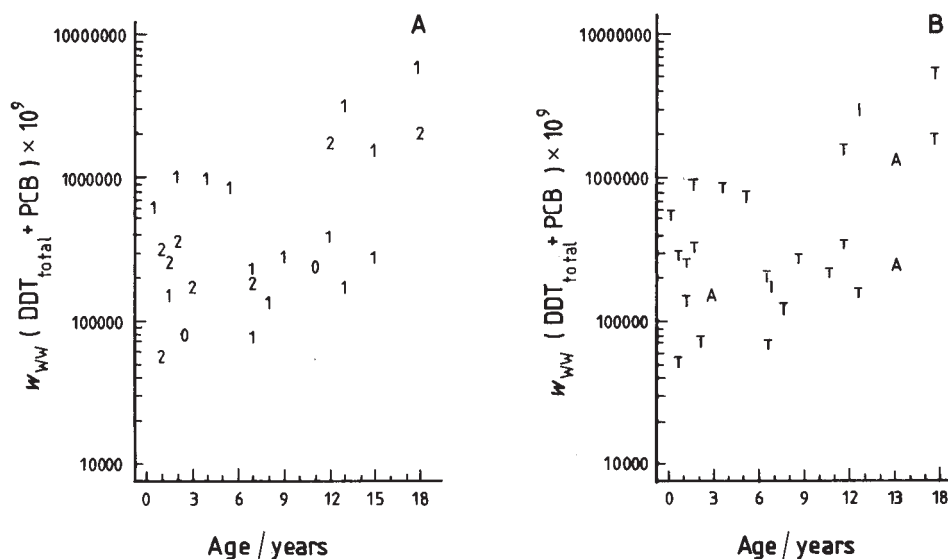


Figure 12. *Stenella coeruleoalba*. Levels of organochlorines in brain, blubber, muscle and liver in relation to age. (A) Showing sex (0: sex unknown, 1: male, 2: female) and cause of death (circle: dolphins dying because of accidents). (B) Showing locality of stranding (T: Tyrrhenian Sea, A: Adriatic Sea, I: Ionian Sea.) (modified from Marsili *et al.*).¹⁷⁵

Bottlenose and Risso's dolphins found dead along the Italian coast in 1992 were analyzed for the presence of PCB isomers and DDT. High levels of PCBs (90–1400 $\mu\text{g g}^{-1}$, wet weight) were detected in the blubber of stranded carcasses.¹⁷⁶ The levels were higher than those found in animals showing reproductive failure and physiological impairment following prolonged PCB exposure, suggesting that the contamination by PCBs as well as DDT may be a major causative factor for the large-scale deaths of dolphins in the Mediterranean Sea. The 2,3,7,8-TCDD toxic equivalents estimated for bottlenose and Risso's dolphins were 18.8 and 20.0 ng g^{-1} , respectively, with a major contribution from mono-*ortho* PCBs. The mono-*ortho* congeners of IUPAC No. 105, 118 and 156 accounted for most of the toxicity exerted by PCBs in these dead dolphins. An increase in the proportion of non-*ortho* coplanar PCB congener of IUPAC No. 169 to No. 126 with an increase in the total PCB concentration in the blubber suggested a strong induction of drug metabolizing enzymes. It is possible to use CB-169/CB-126 concentration ratio to indicate whether there has been a strong activation of cytochrome P-450 enzyme system in severely exposed/contaminated dolphin populations.

BIOMARKERS

It is extremely difficult to quantify the risks associated with xenobiotics, since the single and combined biological effects of most of them are still unknown. The complexity of the problem will increase in the future because the anthropogenic organic compounds introduced into the environment are ever more numerous. Therefore, the optimal approach to the problem of the risk assessment of xenobiotics is measurement of early biological effects induced as a response to the micropollutants pool in the water environment. Biomarkers of contaminant exposure and effect are defined as early changes at the molecular and cellular level of biological organization induced by chemical pollutants. They have obvious utility in rapid environmental screening for problem sites. This permits detailed studies of chemical, biological and ecological effects to be targeted effectively. However, it has become increasingly clear that any definitive assessment of environmental risks must be correlated with the origin and the concentration of the xenobiotics present. To this end, analytical protocols must be designed for the isolation and identification of such compounds, as well as for the application of biomarker assays to environmental samples.^{177,178}

The use of cytochrome P4501A (CYP1A) and other measurements as biomarkers was investigated in the liver of goby (*Z. ophiocephalus*) and the digestive gland of mussel (*M. galloprovincialis*) from several sites in the Venice lagoon as part of the UNESCO-MURST Venice Lagoon Ecosystem

Project.¹⁷⁹ Most tissue contaminants (PAHs, PCBs, DDTs) and biochemical measurements varied seasonally. Elevated 7-ethoxyresorufin *O*-deethylase activity and CYP1A-protein levels in goby were correlated with high tissue contaminant levels at the industrial Porto Marghera site. On occasions, activities of the antioxidant enzymes catalase and putative DT-diaphorase (resorufin reductase activity) in male but not female goby were also higher at Porto Marghera than at other sites, but no differences were seen in superoxide dismutase (SOD) activity. A range of measurements (SOD, catalase, NADPH-cytochrome c reductase and glutathione *S*-transferase activities, P-450 and '418-peak' contents) in mussel showed little difference between sites. However, indications were obtained of elevated levels of CYP1A1-like mRNA, CYP1A-like protein and the metabolism of benzo[*a*]pyrene to free metabolites in mussels from the Venice lagoon compared to a site in the Adriatic Sea. The studies demonstrate the usefulness of CYP1A as a biomarker for organic pollution in fish and indicate some potential for its application in mollusks.

Mussels, *Mytilus galloprovincialis*, were sampled at three times of the year, from various sites within the Venice Lagoon and a reference Platform site in the north Adriatic.^{179, 180} The immune response of the mussels was assessed using a range of assays, which included total and differential cell counts, phagocytosis, degradative enzyme levels and release of reactive oxygen metabolites. Chlorinated hydrocarbons, including lindane, DDT and PCBs, together with trace metal levels were measured in digestive gland tissues from the mussels. The measurements of immune response and the contaminant levels showed seasonal fluctuations. However, the results did demonstrate significant differences in a number of immunocompetence assays which in some instances showed some correlation with the levels of contaminants measured in the tissues. In particular, total and differential cell counts, phagocytosis and release of reactive oxygen metabolites showed a degree of correlation with contaminant burdens though other factors were clearly involved. The results confirm the requirement for using a range of assays for monitoring pollution effects.

Fish belonging to three species of cyprinids, that is, barbel (*Barbus plebejus*), chub (*Leuciscus cephalus*), and Italian nase (*Chondrostoma soetta*), were collected from two sites of the River Po, located upstream and downstream from the confluence of one of its middle-reach polluted tributaries, the River Lambro.¹⁸¹ The two groups of individuals caught for each species were analyzed and compared for several microsomal and cytosolic biochemical markers. The enzymatic activities assayed in fish liver included ethoxyresorufin *O*-deethylase (EROD), aminopyrine *N*-demethylase (APDM), uridine diphosphate glucuronyl transferase (UDPGT), glutathione *S*-transferase (GST), glutathione reductase, and glutathione peroxidase. In addition, the

contents of reduced glutathione and nonprotein thiols were measured. Despite some differences among species, all microsomal activities (EROD, APDM, and UDPGT) were found to be significantly induced in fish living downstream the River Lambro. With the exception of a higher GST enzyme activity of barbel from the downstream reach, no significant modification was evident in any of the tested cytosolic biomarkers. In general, the alterations observed in feral fish are consistent with the results found in previous studies conducted with rainbow trout (*Oncorhynchus mykiss*) under both laboratory and field conditions in the same middle reach of the River Po. All of the data indicate that the downstream tract of the main river is exposed to the load of pollutants transported by the River Lambro, including known inducers such as polychlorinated biphenyls and polycyclic aromatic hydrocarbons.

RISK RELATED TO ACCEPTABLE DAILY INTAKES OF CHLORINATED HYDROCARBONS INTO MAN

Acceptable daily intake (ADI) denotes the dose, expressed on a body weight basis, of a substance which can be accepted over a lifetime without appreciable health risk. The starting point is usually the no observed adverse effect level (NOAEL) estimated in 90-day animal studies and extrapolated to man with some margin of safety.¹⁸² The animal experimental carcinogenicity data are sufficient for DDTs and PCBs. It is widely accepted that in the absence of adequate data on humans, it is biologically plausible and prudent to regard agents for which there is sufficient evidence of carcinogenicity in experimental animals as if they presented carcinogenic risk to humans.¹⁸³ There is a very wide gap between ADI values set by FAO/WHO and the daily intake which assures that the life-time risk attributable to a carcinogenic organochlorine does not exceed the acceptable level. According

TABLE XI

Daily intake associated with 10^{-5} life risk and levels of organochlorines which present the same acceptable risk at three different fish consumption levels (modified from UNEP/FAO/WHO/IAEA, 1990)⁴³

	Daily intake resulting in 10^{-5} risk / $\mu\text{g d}^{-1}$	Levels ($w \times 10^9$) in seafood with 10^{-5} risk		
		One meal weekly	Three meals weekly	One meal daily
DDTs	0.083	4.2	1.4	0.55
PCBs	0.158	8	2.6	1.0

to WHO,¹⁸⁴ the risk is acceptable if not more than one in every 100 000 people (10^{-5} risk) develop cancer as a result of life-time exposure to a carcinogen. The choice of 10^{-5} as an acceptable or reference risk level has been based on an arbitrary or default assumption.

Table XI shows daily intakes associated with 10^{-5} life-time risk. The table also shows the maximum organohalogen levels, which, if there were no other sources of exposure (from the atmosphere, dust, other foodstuffs), could keep intake at the acceptable risk level for low, medium and high fish consumption.

Table XII shows risk associated with the consumption of fish in the low, medium and high contamination categories. Though these numbers are alarming, they must be considered in perspective. First of all, evidence of carcinogenicity in animals is not a proof of carcinogenicity in man, but based on animal experiments it is prudent to regard PCBs and DDTs as potential human carcinogens. In the case of PCB, this view is supported by limited evidence of human carcinogenicity.¹⁸⁴

Polychlorobiphenyls have been determined in samples of milk and butter from areas of Italy reflecting different environmental pollution, in one sample of a local Italian diet, and in samples of agricultural soil.¹⁸⁵ PCBs were determined as single congeners and their contamination was represented as a pattern including a maximum of 48 different congeners, containing from three to seven chlorine atoms.

The migration of PCBs from a waste dump into the karstic groundwater and source water of the Kupa River in Slovenia has been established. An investigation of the levels of chlorinated hydrocarbons in tap water and water and fish samples collected from 1985 to 1988 from the Kupa River in the region of Petrinja and Sisak (about 200 km downstream from the primary

TABLE XII

Conseccion between organochlorine contamination in seafood and life-time cancer risk (modified from UNEP/FAO/WHO/IAEA, 1990)⁴¹

Levels ($w \times 10^9$)		Cancer risk		
		One meal weekly	Three meals weekly	One meal daily
DDTs	8	1.9×10^{-5}	5.8×10^{-5}	1.4×10^{-4}
	50	1.2×10^{-4}	3.6×10^{-5}	9.0×10^{-5}
	150	3.6×10^{-4}	1.1×10^{-3}	2.7×10^{-3}
PCBs	25	3.2×10^{-5}	9.5×10^{-5}	2.4×10^{-4}
	150	1.9×10^{-4}	5.6×10^{-4}	1.4×10^{-3}
	450	5.7×10^{-4}	1.7×10^{-3}	4.3×10^{-3}

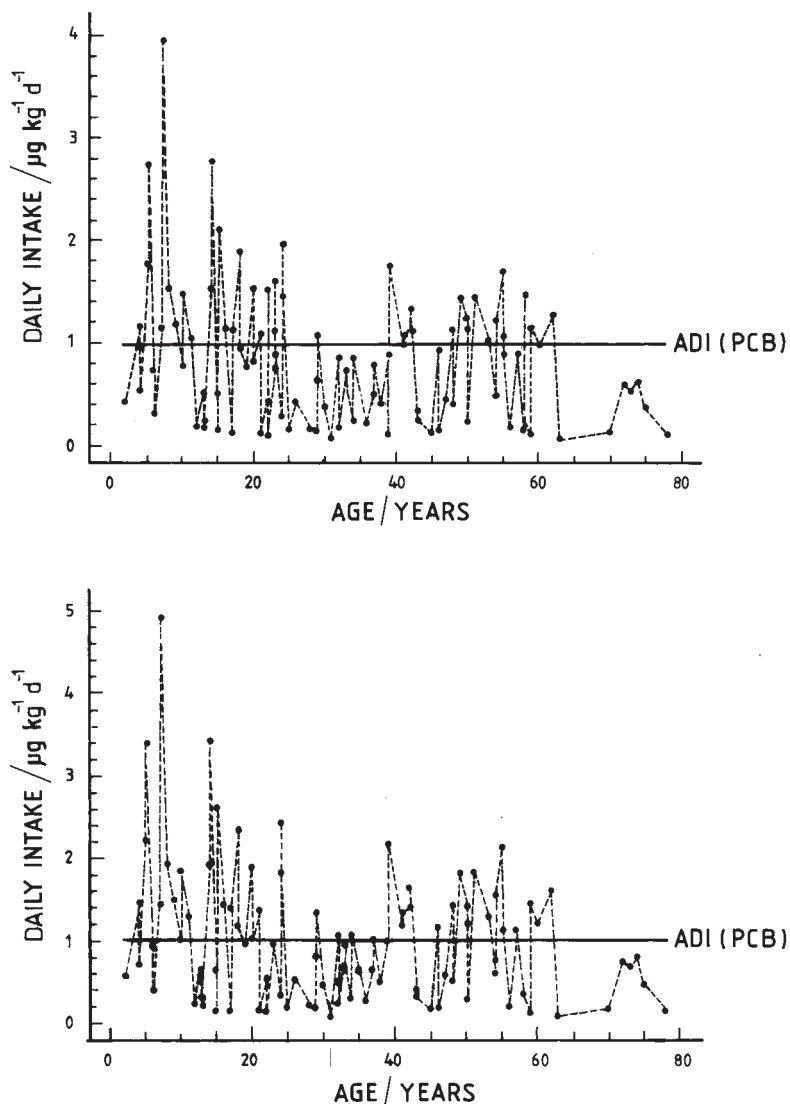


Figure 13. Daily intake of PCBs by sport fishermen and their family members in the Zadar area, according to age. Upper figure: fish consumption of the total investigated area of Zadar. Lower figure: fish consumption of the Marina Station only.

contaminated area) was performed. Daily PCB and DDT intake was studied among sports fishermen and their families who consume fish from the Kupa River in significant quantities. The same calculations were performed for sports fishermen and their families in the Zadar area. In Figure 13, the

daily intake of PCBs by sports fishermen and their family members in the Zadar area, is presented according to age. Upper figure – fish consumption from the total investigated area of Zadar. Lower figure – fish consumption from the Marina Station. As seen, there are many persons (especially those assumed to consume fish caught from the Marina Station) who ingest more than the acceptable daily PCB intake, ADI, ($1 \mu\text{g kg}^{-1} \text{d}^{-1}$).¹²¹

Studies of workers exposed to high doses of PCBs over long periods of time have not demonstrated an increased cancer risk.¹⁸⁶ In fact, the only health effects that could be attributed to PCBs were skin and eye irritation. Recent studies of the possible effects of prenatal exposure to PCBs on neuro-development in infants and children have been criticized for methodological deficiencies. There is no conclusive evidence that PCB levels in the general population are causing intellectual deterioration in children exposed in utero. Some investigators have also suggested that PCBs and other chemicals in the environment can interfere with the body's endocrine system, leading to infertility, certain types of cancer and other hormone-related disorders. Evidence for estrogenic effects of environmental PCBs remains weak and circumstantial.¹⁸⁶

CONCLUDING REMARKS CONCERNING THE LEVELS OF ORGANOCHLORINE COMPOUNDS IN THE ADRIATIC AND THE MEDITERRANEAN

The analytical uncertainty of chlorinated hydrocarbons in marine samples makes the evaluation of and comparison between the data of different authors very difficult. Intercalibration exercises show a large dispersion of results. The different areas of the Mediterranean have been surveyed very unevenly. Some data were obtained from only one or two sites (air, rain, waste waters) in the entire Mediterranean. Even for some biota samples (for instance mussels and *Mullus barbatus*) for which there are plenty of data, the scatter of sampling between regions in the Mediterranean Sea is very uneven. With the exception of Israel and Turkey, very few data are available from the southern and eastern coasts of the Mediterranean.

As a measure of the »quality« of all available data and also to see how representative these data are for the investigated area, Table XIII gives the DDT total and PCB level ratios for water, sediment, mussels and striped mullet from the Mediterranean Sea per regions. Average levels were calculated using data for the period from 1970 to 1984 (but mainly from 1976/1979 period) obtained by all the various research groups that have published data. There are very large differences for many »level factors«. For instance, only 300 for DDT total between sediment/water in area IV and 142 000 for area VIII. Similarly, large differences are obtained by comparing level factors for

TABLE XIII
DDT and PCB levels ratios between various matrices from the Mediterranean Sea (modified from UNEP/FAO/WHO/IAEA, 1990)⁴³

Area ^a	Sediment ^b / water		Mussels ^c / water		Fish ^c / water		Mussels ^c / sediment ^b		Fish ^c / sediment ^b		Fish ^c / mussels ^c	
	DDTs	PCBs	DDTs	PCBs	DDTs	PCBs	DDTs	PCBs	DDTs	PCBs	DDTs	PCBs
II	NA ^d	17.8 × 10 ³	NA	14.4 × 10 ³	NA	1.6 × 10 ³	6.6	2.1	12.2	7.9	1.9	3.8
III	NA	0.4 × 10 ³	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
IV	0.3 × 10 ³	44.3 × 10 ³	2.8 × 10 ³	41.7 × 10 ³	4.3 × 10 ³	62.6 × 10 ³	8.1	0.9	12.3	14.0	1.5	1.5
VI	NA	21.2 × 10 ³	NA	43.3 × 10 ³	NA	15.0 × 10 ³	3.2	2.0	1.8	0.7	0.6	0.3
VII	NA	0.9 × 10 ³	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
VIII	142.2 × 10 ³	10.3 × 10 ³	26.7 × 10 ³	255.3 × 10 ³	84.4 × 10 ³	28.8 × 10 ³	0.2	2.5	0.6	2.8	3.2	1.1
IX	NA	NA	NA	NA	NA	NA	NA	NA	10.2	0.9	NA	NA
X	NA	5.5 × 10 ³	NA	NA	NA	15.0 × 10 ³	NA	NA	10.7	27.3	NA	NA
Adriatic	1.3 × 10 ³	21.7 × 10 ³	7.6 × 10 ³	28.8 × 10 ³	6.1 × 10 ³	21.7 × 10 ³	4.9	4.6	3.7	0.8	0.7	0.9

^aSee Figure 4.

^bSediment: dry weight.

^cMussels, fish (*Mullus barbatus*): wet weight.

^dNA, not applicable.

TABLE XIV

»Pollution order« of the Mediterranean Sea areas with DDTs and PCBs calculated on the basis of published average levels of these pollutants in water, sediment, mussels and fishes^a (modified from UNEP/FAO/WHO/IAEA, 1990)⁴³

DDTs			Points ^b		PCBs			Points		DDTs + PCBs			Points
Order	Area ^c	No. of matrices	Order	No. of matrices	Order	Area	No. of matrices	Order	No. of matrices	Order	Area	No. of matrices	Points
1.	VIII	5	14.8	1.	1.	II	5	22.6	1.	1.	II	9	35.5
2.	IX	2	12.4	2.	2.	VIII	5	20.2	2.	2.	VIII	10	35.0
3.	II	4	12.9	3.	3.	IV	6	19.2	3.	3.	IV	12	29.7
4.	Adriatic	5	11.0	4.	4.	Adriatic	5	16.4	4.	4.	Adriatic	10	27.4
5.	IV	6	10.5	5.	5.	VI	6	12.6	5.	5.	VI	11	21.5
6.	VI	5	8.9	6.	6.	III	2	11.1	6.	6.	III	3	18.1
7.	III	1	7.0	7.	7.	X	3	6.2	7.	7.	IX	4	16.2
8.	X	2	3.6	8.	8.	VII	2	2.8	8.	8.	X	5	9.8
9.	VII	1	1.0	9.	9.	IX	2	2.8	9.	9.	VII	3	3.8

^a*Mullus barbatus*, *Engraulis encrasicolus* and *Thynnus thynnus*.

^bCalculation of »points« is described in text.

^cSee Figure 4.

mussel/water: 2800 for DDTs in region IV but 255 000 for region VIII, *etc.*, *etc.* These differences are probably not only a consequence of analytical problems but also of a very large scatter in the levels of the investigated pollutants from region to region and, especially for sediments and mussels, also within a region. There are also differences between level ratios for fish/sediment and mussel/fish but they are not so large as for other compartments.

In order to obtain some measure of the quantitative relationship between investigated regions, a »pollution order« was calculated for the following matrices: water, sediment, mussels and fishes *Mullus barbatus*, *Engraulis encrasicolus* and *Thunnus thynnus* (Table XIV). Because even for these relatively »popular« matrices there is considerable scatter among the data, the number of »points« was divided by the number of regional data. For instance, DDT total in water was measured in three regions. As seen from the presented results, the highest value of averages is in region IV. Points were calculated $3 \cdot 3/9 = 1$. The second one is region V (The Adriatic Sea) and it was obtained: $2 \cdot 3/9 = 0.7$ *etc.* For instance mussels were analyzed in five regions and the highest averages were obtained for DDT in region II, hence the mean points are $5 \cdot 5/9 = 2.8$. All the calculations were made in this way and the results are presented with the »order« of pollution levels separately for DDTs and together with PCBs as summed in Table XIV. It has to be stressed that for areas marked 1 to 5 the reliability is probably relatively good because similar numbers of data are available for each matrix.

Comparing the averages of DDT levels in sediments, mussels and three fish species (*Mullus barbatus*, *Engraulis encrasicolus* and *Thynnus thynnus*) of the whole Adriatic with the averages of the levels of these pollutants in the other areas in the Mediterranean, it can be concluded that in three areas of the Mediterranean Sea (Ionian and Aegean sea, Northeast Mediterranean and Balearic sea) levels are higher and in 5 areas (Ligurian sea, Thyrrenian sea, Southwest Mediterranean, Southeast Mediterranean, and South-central Mediterranean) DDT levels are lower. Levels of PCBs in these samples are higher in three areas of the Mediterranean region (Balearic sea, Ionian and Eagan sea, Ligurian sea) in comparison with the Adriatic and in five areas (Thyrrenian sea, Southwest Mediterranean, Southeast Mediterranean, South-central Mediterranean and Northeast Mediterranean) levels of PCBs are lower.

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ABBREVIATIONS

- 2,3,7,8-TCDD = tetrachlorodibenzodioxine
 ASCOP = Adriatic Sea Cooperation Programme
 BHC = benzenehexachloride
 BOD₅ = biological oxygen demand in 5 days
 CBs = chlorinated benzenes
 ECE = European Commission for Environment
 EPA = US Environmental Protection Agency
 FAO = Food and Agriculture Organization
 GESAMP = Group of Experts on Environmental Pollution
 HCB = hexachlorobenzene
 HCH = hexachlorocyclohexane
 IAEA = International Atomic Energy Agency
 IAEA MEL = Monaco Laboratory of IAEA
 IARC = International Agency for Research on Cancer
 LABs = linear alkylbenzenes
 MED POL = Mediterranean Action Plan: Pollution Monitoring and Research Programme
 mRNA = messenger ribonucleic acid
 PAHs = polycyclic aromatic hydrocarbons
 PCDD/Fs = polychlorinated dibenzodioxines and polychlorinated dibenzofuranes
 PCDDs = polychlorinated dibenzodioxines
 PCDFs = polychlorinated dibenzofuranes
 PCNs = polychlorinated naphthalenes
 UNEP = United Nations Environment Programme
 UNESCO = United Nations Educational, Scientific and Cultural Organization
 WHO = World Health Organization

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SA TA

PCB i DDT adrans r

Mladen Picer

Dan je pregled razvoja analize DDT i PCB u moru, uključujući obradbu uzoraka, čišćenje, identifikaciju i kvantitativno određivanje plinskom kromatografijom. Autor je, s naglaskom na probleme vezane uz morske ekosustave, detaljnije raspravljao o pouzdanosti objavljenih podataka o razinama istraživanih zagađivala u Jadranu.

Sudbina kloriranih ugljikovodika u morskom ekosustavu diskutirana je s obzirom na vezanje ovih spojeva na čestice i dinamiku u ekosustavu obalnog mora. Nadalje je diskutirano hidrofobno vezivanje zagađivala s površinama te njihova ugradnja, agregacija i kruženje u morskom ekosustavu. Prikazane su razine koncentracije DDT i PCB u zraku, kišnici, vodi, sedimentima, planktonu, školjkašima, rakovima i drugim morskim organizmima, uključujući morske ptice i sisavce Jadrana, te u usporedbi s razinama tih spojeva u Mediteranu. Uglavnom se vide tendencije smanjenja (osobito DDT), ali i nadalje postoje određeni lokalni izvori zagađivanja tim spojevima. Autor je prikazao neke radove o korištenju biomarkera kao pogodnih bioloških indikatora za ocjenu rizika od kloriranih spojeva, kao i drugih organskih mikrozagađivala u Jadranu. Opisana su istraživanja rizika unosa PCB i DDT iz mora u kritične grupe stanovništva konzumacijom plodova mora zagađenih tim spojevima.